FLUORODINITROETHANOL AND DERIVATIVES*

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Introduction

The chemistry of 2-fluoro-2,2-dinitroethanol has been investigated for the past several years, and it is a privilege to present some of this material at this time. This paper presents a summary of a process evaluation study, and much of the chemistry involved will be reported in greater detail by the original authors in the coming months. It may be stated at the outset that the chemistry of fluorodinitromethyl compounds shows marked similarity to trinitromethyl or gem-dinitromethyl compounds, which are well-known in the literature.

Synthesis of 2-Fluoro-2,2-dinitroethanol

One preparative method for 2-fluoro-2,2-dinitroethanol (FDNE) is based on the fluorination of the aci-sodium salt of dinitroethanol

$$F_2 (\text{or } ClO_3F) + \begin{matrix} NO_2^{\ominus}Na^{\oplus} \\ | \\ C - CH_2OH \\ | \\ NO_2 \end{matrix} \longrightarrow \begin{matrix} NO_2 \\ | \\ FC\ CH_2OH \\ | \\ NO_2 \end{matrix} \qquad (1)$$

I

The starting material for Reaction (1) is prepared *in situ* by the deformylation of 2,2-dinitro-1,3-propanediol with one mole of base

$$\begin{matrix} NO_2 \\ | \\ HOCH_2C\ CH_2OH \\ | \\ NO_2 \end{matrix} + NaOH \longrightarrow \begin{matrix} NO_2^{\ominus}Na^{\oplus} \\ | \\ C\ CH_2OH \\ | \\ NO_2 \end{matrix} \qquad (2)$$

II

Compound II is preferably prepared by the oxidative nitration of 2-nitro-1,3-propanediol (Reference 1). II is not isolated, but is partially purified by extraction from the aqueous reaction mixture with ethyl or isopropyl ether, followed by an extraction of the ether solution with aqueous base, which converts II to the aci-sodium salt of dinitroethanol. Although other methods of preparation of II are known, the route shown was the one of choice.

Conversion of II to FDNE was carried out by introducing fluorine gas, diluted 1:1 with nitrogen, into the aqueous solution of the aci-sodium salt at 15 to 25° (Reference 2). It was found that efficient dispersion of the fluorine is essential, and that stainless steel gas-inlet tubes with open ends of 1/4 or 3/8 in., or with various hole sizes of 0.016 to 0.040, are satisfactory in a 50-liter vessel. The smaller the diameter of the holes, however, the more frequently were they occluded by sodium fluoride. A rapid injection of water served to remove the obstruction.

* This report is based on work supported, in large part, by the AEC through the Lawrence Radiation Laboratory of the University of California.

Yields of 60 to 70% of FDNE were generally obtained, although about 100% of the theoretical quantity of fluorine was consumed. The pH of the solution was not a critical factor, so long as it was maintained at or above the 7.5 to 8.0 level. The same results were obtained whether the pH was maintained at 8.0 or whether fluorination was begun at a pH of about 11, and the solution allowed to go acid; in the latter case, however, it was sometimes necessary to add alkali and to continue the fluorination.

Ethyl ether was found to be very efficient in extracting FDNE from the aqueous fluorination mixture. However, it tends to extract some impurities along with the FDNE. For example, one of the contaminants found in the fluorination of II was identified as 2,2,4,4-tetranitro-1,5-pentanediol (Reference 3). It was obtained in rather significant quantity (3 to 5 percent) from an ether extract of FDNE, from a batch in which most of the FDNE had previously been extracted with methylene chloride. In actual practice, sodium chloride is added to decrease the solubility of FDNE in the aqueous medium, and methylene chloride, with a far less favorable distribution coefficient than ether, is used as the extractant. The crude product obtained by removing the solvent is generally 80 to 90 mole-percent pure, as analyzed by gas chromatography.

An alternate method for preparing FDNE consists of the fluorination of nitroform, followed by reduction with alkaline peroxide and the Henry reaction with formaldehyde (References 2 and 4).

$$HC(NO_2)_3 + F_2 \xrightarrow{OH^\ominus} FC(NO_2)_3 \qquad (3)$$

III

$$FC(NO_2)_3 + H_2O_2 + HCHO \xrightarrow{OH^\ominus} FDNE \qquad (4)$$

The fluorination of nitroform is carried out under conditions similar to those described for the aci-sodium salt of dinitroethanol, but the yields are superior (80 to 90% of theory), and the isolation of the product presents little difficulty; III is essentially insoluble in water, and, following mild washing, is obtained in 98 mole-percent purity (gas chromatography). A slight source of difficulty is presented by the emulsified interface, but this problem can be overcome by vacuum filtration and water-washing. Nitroform starting material may, if necessary, be prepared by the alkaline-peroxide reduction of tetranitromethane, and fluorinated <u>in situ</u>; in this case, yields of III from 65 to 70% (based on tetranitromethane) are obtained.

The route shown in (4) was discovered by workers at the U.S. Naval Ordnance Laboratory and substantial improvements since then, primarily by NOL, have made the process a very attractive one. The reduction of III, when carried out at -5 to -10°C in alkaline medium with a 20% excess of hydrogen peroxide and formaldehyde, gives yields of 90% FDNE in 95 mole-percent purity. The reaction can be effected in aqueous methanol in order to enhance the solubility of FTM in the reaction mixture, or, alternatively, a surface-active agent such as sodium p-tolunesulfonate or Triton X-100*, may be added to achieve the same result. The latter method is particularly advantageous when it is desired to use the solution of FDNE in the methylene

* An alkyl phenoxy polyethoxyethanol (Rohm & Haas Co.)

chloride extractant without other hydroxyl-containing impurities; water alone is readily removed from the solution, but a significant quantity of methanol, together with the attendant water, presents a more tedious problem.

Physical Characteristics of FDNE

Fluorodinitroethanol is a mobile, colorless liquid, b.p. 53° at 1 mm Hg, m.p. 9 to 10-1/2°C. Its density is 1.54 g/cc at 25°C. It can be vacuum-distilled with very minor decomposition (much less than 1%), but that slight decomposition does occur is indicated by small deposits of paraformaldehyde. Its refractive index is 1.4330 (n_D^{25}). It is a very strong vesicant, and skin contact is to be avoided. Values of its sensitivity to impact or shock are not very consistent, but certain evidence suggests that caution is in order. For example, a 70 weight-percent solution in methylene chloride had an impact sensitivity of less than 10 cm compared to 50 cm for neat FDNE (Olin Mathieson Tester, 2 Kg weight, 50% point; n-propyl nitrate = 8 cm).

Analysis of FDNE

Analysis of FDNE may be based on several criteria, of which purity by gas-chromatography is perhaps the most useful. Consistent results have been obtained with a 6-ring polyphenyl ether column in an Aerograph A90 gas chromatograph. An Aerograph Model 325 temperature programmer was attached to the oven heater, and by programming from 90 to 140°C at 6°C/min, very satisfactory separation of components was achieved.

FDNE may also be analyzed by measuring its absorbancy in dilute aqueous base at 382 mμ. For pure FDNE, log ε = 4.27. This determination must be made on fresh solutions, as the anion of fluorodinitromethane reacts with hydroxide ion.

A third method of analysis was developed by titration of FDNE in acetonitrile with 0.1N tetrabutylammonium hydroxide. Under these conditions, FDNE titrated as a dibasic acid, giving a single, sharp inflection.

Synthesis of bis(2-Fluoro-2,2-dinitroethoxy)methane

One of the more interesting derivatives of FDNE is its formal, bis(2-fluoro-2,2-dinitroethoxy)methane (FEFO) (Reference 5). Since conventional methods of acetal formation fail with electronegatively substituted alcohols such as trinitromethyl, gem-dinitro, and fluorodinitromethyl compounds, recourse was had to a method first developed at NOL (Reference 6), involving the use of concentrated sulfuric acid as the reaction medium

$$2x\ FC(NO_2)_2CH_2OH + (HCHO)_x \xrightarrow{H_2SO_4} x\ \underset{\text{IV (FEFO)}}{\left[FC(NO_2)_2CH_2O\right]_2CH_2} \qquad (5)$$

Under these conditions, FEFO is produced in 70 to 90% yields. The reaction may conveniently be carried out by adding concentrated sulfuric acid slowly to a solution of FDNE and s-trioxane in methylene chloride, but many variations yield equally satisfactory results. In place of trioxane, paraformaldehyde may be used, and the methylene chloride may be replaced by a similar solvent, or the reaction may be effected without the use of organic solvent by adding FDNE to a solution of formaldehyde (from either trioxane or paraformaldehyde) in sulfuric acid. A solvent may then be employed to assist in the isolation and purification of the product.

The effects of an excess of formaldehyde or an excess of FDNE on the yield and purity of FEFO were assessed in a series of runs in which the molar ratios of FDNE to formaldehyde were 2.5:1.0, 2.0:1.0, and 1.5:1.0, respectively. An additional run was made at the 2.0:1.0 ratio, in which the condensation medium was 100% sulfuric acid in place of the usual 95 to 98% acid. The results are summarized in Table 1.

TABLE 1

VARIATION OF REACTANT RATIO IN FEFO SYNTHESIS

Case No.	Molar Ratio, FDNE:HCHO	% FEFO*	% Impurity of Higher GC Retention Time	% Yield
1	2.5:1.0	99.2	0.8	88.0
2	2.0:1.0, conc H_2SO_4	98.2	1.8	82.9
3	2.0:1.0, 100% H_2SO_4	98.9	1.1	79.0
4	1.5:1.0	93.6	6.4	83.5

* GC assay

It is apparent that the reagents in stoichiometric ratio will yield good FEFO very effectively; that the higher purity FEFO obtainable with 100% sulfuric acid may compensate for the use of slightly less pure FDNE; and that even a 25% excess of formaldehyde can be tolerated, provided purification with sulfuric acid is added to the process (see below).

A series of runs (all with molar ratio 2.0:1.0) in which the reaction temperature was maintained for two hours at 0 to 10°C, 20 to 25°C, and 35 to 40°C, gave yields of 87.3, 87.8, and 84.0% FEFO, respectively, all of identical quality. The run at the highest temperature was carried out primarily to determine what, if anything, might occur if the reaction went out of control. Since methylene chloride served as the organic solvent in these runs, it apparently served to control the exotherm. This series further showed that product yield and purity are unaffected by reaction temperatures from 0° to at least 25°C.

In practice, the preparation of FEFO can be carried out conveniently by using the solution of FDNE in methylene chloride directly, without isolating the FDNE, although the solution is generally dried by passing through a silica gel-Drierite column, and a portion of the solvent is removed by distillation to avoid handling excessive volumes. The requisite amount of s-trioxane is then added to the solution, and concentrated sulfuric acid (approximately 1 ml acid per gram of FDNE) is then added dropwise with good agitation at 20 ± 5°C. The reaction mixture is stirred an additional 1 to 2 hours, and the methylene chloride (upper) layer is separated. The FEFO solution is then washed countercurrently or batchwise with 5% aqueous sodium hydroxide, and dried by percolation through a column of silica gel. Removal of the solvent under vacuum leaves the product as a clear, colorless liquid, generally 90 to 98 mole-percent pure, as analyzed by gas chromatography.

The contaminants in FEFO generally consist of several products of lower GC retention-times, and one or two of higher retention times.* The latter have been

* Referred to, for convenience, as "high-boilers"

identified (Reference 7) as the FEFO analogs with two and three methyleneoxy chains in the molecule, respectively.

$FC(NO_2)_2CH_2OCH_2OCH_2OCH_2CF(NO_2)_2$ and $\left[FC(NO_2)_2CH_2OCH_2O\right]_2\ CH_2$

V VI

Compounds V and VI seem to arise whenever the condensation medium is contaminated with water. If one is aware of this beforehand, the problem can be overcome by the use of fuming sulfuric acid, as shown in Table 2.

TABLE 2

EFFECT OF DILUTION WITH WATER ON FEFO SYNTHESIS

Case No.	Conditions	Mole-% Components with lower GC retention time	% FEFO	% High-boilers	% Yield
5	Standard*	3.6	93.4	3.0	92.5
6	10% H_2O added to FDNE	4.3	44.7	51.0	83.6
7	As in 93, with 20-23% fuming H_2SO_4 in place of conc. H_2SO_4	2.9	93.4	3.7	77.7

* 2.0 moles of FDNE (distilled) per mole of formaldehyde

Results similar to those of Case No. 6 are obtained whenever the FDNE-methylene chloride solutions are inadequately dried.

If the FEFO product is still too highly contaminated with V and/or VI, purification may be effected by low-temperature crystallization from methylene chloride-hexane in a tedious, somewhat wasteful procedure, or by agitation with concentrated sulfuric acid. Results from the latter treatment are presented in Table 3.

TABLE 3

PURIFICATION OF FEFO WITH SULFURIC ACID

Case No.	Mole-% Components with lower GC retention time	% FEFO	% High-Boilers V	% High-Boilers VI	% Recovery
8, crude	1.2	87.3	5.6	5.9	-
8, purified	1.7	96.6	0.1	1.6	82
9, crude	0.7	95.6	3.7	-	-
9, purified	1.4	98.6	-	-	89

Extremely interesting results were obtained in the course of preparing FEFO from an FDNE-methylene chloride solution after attempted purification. This FDNE was prepared from fluorotrinitromethane in methanolic solution, and the FDNE-methylene chloride solution was later found to be highly contaminated with methanol and water. The crude FEFO-methylene chloride solution, following separation from the sulfuric acid layer, was divided into two equal portions. One portion was worked up in the usual manner, and the other was treated with two portions of concentrated sulfuric

acid before being worked up. The first portion gave a yield of 48 percent (calculated as FEFO), the second 42 percent. GC analysis showed the following results:

TABLE 4

IN-PROCESS PURIFICATION OF FEFO WITH SULFURIC ACID

Case No.	Mole-% Components with lower GC retention time	% FEFO	% High-Boilers V	% High-Boilers VI
10, treated as usual	17.1	37.6	43.8	1.5
10, purified in process	1.0	93.7	5.3	-

In spite of the fact that the conventionally-treated FEFO was apparently not completely freed of solvents, and the results are thus not strictly comparable, it is evident that a very high degree of purification was achieved. Since the yield of FEFO was nearly the same in both cases, it must be concluded that purification took place primarily other than through extraction of V and VI, and that the latter may have been converted into FEFO by a process indicated in the following sequence:

$$ROCH_2OCH_2OR + H^{\oplus} \rightleftharpoons ROCH_2\overset{H}{\overset{\oplus}{O}}CH_2OR \quad (6)$$

$$ROCH_2OCH_2OR \rightleftharpoons \left[ROCH_2^{\oplus}\right] + HOCH_2OR \rightleftharpoons ROH + HCHO$$

$$\left[ROCH_2^{\oplus}\right] + ROH \rightleftharpoons (RO)_2CH_2 + H^{\oplus}$$

The purification of FEFO with concentrated sulfuric acid immediately following separation of the FEFO-methylene chloride solution from the sulfuric acid reaction medium has consistently removed nearly all of the high-boiling contaminants, and has been made a standard procedure in FEFO preparation.

Several routes are known which yield FEFO from intermediates other than FDNE. One of these methods utilizes bis(2,2,2-trinitroethoxy) methane (VII) as the starting material (Reference 4)

$$\underset{\text{VII}}{\left[(NO_2)_3CH_2O\right]_2CH_2} \xrightarrow[H_2O_2,OH^{\ominus}]{} \underset{\text{VIII}}{\left[(NO_2)_2C^{\ominus}CH_2O\right]_2CH_2} \xrightarrow{F_2} \text{FEFO} \quad (7)$$

VII is reduced to the disodium salt (VIII) in the presence of alkaline peroxide in aqueous methanol. The organic solvent, added initially to ensure solubility and facilitate reaction of the starting material, must then be removed by vacuum distillation prior to fluorination. The product has been obtained in yields of up to 60% by this route. The sensitivity of VII, and the fact that large volumes and much time are required to effect the removal of the methanol, are severe disadvantages in this process.

Moderate yields of pure FEFO are obtained via another route which utilizes VII as the starting material:

$$\text{VII} \xrightarrow[H_2O_2,OH^{\ominus}]{} \text{VIII} \xrightarrow[H^{\oplus},HCHO]{} \underset{\text{IX}}{\left[HOCH_2C(NO_2)_2CH_2O\right]_2CH_2} \xrightarrow{OH^{\ominus}} \text{VIII} \xrightarrow{F_2} \text{FEFO} \quad (8)$$

The conversion of VIII, by means of the Henry reaction, to bis(3-hydroxy-2,2-dinitropropoxy)methane serves as a means of purification, and as a result the yields from IX

to FEFO are quite high (80 to 85%). The overall yield starting from VII, however, is 45 to 55%, and the large volumes and lengthy procedures decrease the utility of this method even further.

Physical Characteristics of FEFO

FEFO is a colorless liquid, b.p. 120 to 124°C at 0.3 mm Hg, m.p. 14°C. Its density is 1.595 g/cc at 25°C, and its index of refraction $n_D^{25} = 1.4398$. It is soluble in the lower aliphatic alcohols and esters, and in most chlorinated solvents. It is stable to strong acids, and relatively stable to dilute aqueous alkali. Its sensitivity to impact has given values ranging from 11 cm (50% point, 2 Kg weight, RDX = 28 cm) to 40 to 50 cm (50% point, 2.5 Kg weight). Toxicity data are scanty but tend to indicate relatively low toxicity, at least by external exposure to skin or eye.

Analysis of FEFO

Gas chromatography has been employed as the most suitable analytical method for FEFO assay. GC FEFO analyses are conducted with a six ring polyphenyl ether column and a sensitive flame ionization detector. A 2-minute isothermal run at 100°C is followed by a programmed increase of 6°C/minute to 200°C, and an additional 8 minutes at 200°C. All components are eluted within a 20-minute period. These operating conditions give well-resolved peaks with minimal tailing. Although sample sizes have been varied between 0.2 and 0.8 µl, 0.2 to 0.3 µl is preferred.

Preliminary studies suggested that chromatograph oven temperatures between 180 and 200°C would not cause measurable decomposition of FEFO. Therefore, to enhance volatilization and peak shape, a pre-heater temperature of 185°C was selected. However, at this temperature the area percents of the more volatile components did not reproduce well, although consistent data were obtained for the other impurities. A later series of tests of vaporizer temperatures from 150 to 200°C demonstrated the necessity of operating at 150°C because of an apparent degradation of FEFO at the higher temperatures. The data suggest that the apparent increase in impurities of low retention time at temperatures above 150°C is actually due to degradation of FEFO. Its assay decreases with the increase of these impurities attendant with the increased temperatures. By operating the vaporizer at 150°C, reproducible chromatograms are obtained without noticeably altering the elution times.

The anhydrous potentiometric titration applicable to FDNE may be used for FEFO also. FEFO can be titrated in acetonitrile with tetrabutylammonium hydroxide to give a single well-defined break corresponding to the removal of four protons per mole. A single sample assayed 88.8% FEFO, compared with 86.7% obtained by gas chromatography. Since the impurities in FEFO are also apt to have acidic properties, this method was not developed further.

Acknowledgment

The author wishes to express his appreciation to Dr. M. J. Kamlet and Dr. H. G. Adolph of the U.S. Naval Ordnance Laboratory, White Oak, Maryland, and to Dr. K. Baum, Dr. V. Grakauskas, and Dr. F. E. Martin of the Aerojet-General Corporation for permission to present certain information prior to their own publications.

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RECENT CHEMISTRY OF THE OXYGEN FLUORIDES

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Some of the recent chemistry of the oxygen fluorides will be discussed. The reaction of OF_2 and SO_3 has been studied by using O^{17} labeled starting materials and O^{17} NMR spectroscopy, and evidence for an OF transfer mechanism is presented. Similar experiments with O^{17} labeled SO_2 and O_2F_2 have shown that the reactions of O_2F_2 can be explained in terms of an OOF transfer. The generality of this reaction is shown in that $CF_3CF(OOF)CF_3$ and $CF_3CF_2CF_2OOF$ are formed by the reaction of O_2F_2 and $CF_3CF{=}CF_2$.

GAS GENERATOR PROPELLANTS

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The properties of ammonium perchlorate have made it the oxidizer of choice for composite solid propellants for the past 20 years. Its ability to produce propellant compositions with high flame temperatures and densities has made it extremely useful to the missile propulsion industry. Recently, it has become possible to convert this versatile oxidizer to another missile system application, that of warm gas generator propellants.

Warm gas generator propellants are required for driving turbine-alternator systems for electrical power generation, for actuating jet-controlled attitude control systems, and for propelling torpedo propulsion units. Despite the advantages of ammonium perchlorate, it has been difficult to utilize it in these applications, because of the inherently high flame temperature (4500° to $5500^{\circ}F$) of propellants based on it. Because of the materials of construction used in warm gas generator systems, the flame temperatures of these propellants are limited to values in the region of 2200° to $2300^{\circ}F$.

In propellant technology, reduction of flame temperature is most conveniently obtained by reducing the oxidizer to fuel (O/F) ratio to a very low value, so that the composition is extremely fuel rich. In Figure 1 a plot is shown of flame temperature versus the weight percent of NH_4ClO_4 for a mixture of ammonium perchlorate and a typical low oxygen content, high fuel content polymeric hydrocarbon binder. Although aluminum powder is normally used as a fuel component in solid propellants, it has been omitted for two reasons: it increases flame temperature to still higher (and undesirable) values, while producing solid Al_2O_3 particles as an exhaust component. For most gas generator systems, the presence of solid particles in the combustion products is extremely undesirable because of the resultant clogging and erosion of the metallic portions of the system.

Examination of Figure 1 shows that the gradual reduction of the NH_4ClO_4 content from 90% to 70% reduces the flame temperature from $5000^{\circ}F$ down to the desired level of $2200^{\circ}F$, simply by greatly reducing the oxidation ratio of the system. The oxidation ratio decreases from 4.33 down to 1.15 for these two compositions, where oxidation ratio is defined as:

$$\text{Oxidation Ratio} = \frac{\Sigma O \text{ Atoms}}{\Sigma C \text{ Atoms} + \frac{1}{2} \Sigma H \text{ Atoms}}$$

Unfortunately, this reduction results in undesirably high levels of solid carbon in the combustion products when these are exhausted to the atmosphere. This can be seen in Table 1, where the level for the high fuel content binder is 6.45% solid carbon by weight. No carbon is found in the combustion chamber at 1000 psia, but expansion of the gases to 14.7 psia results in copious quantities of black smoke.

Two methods are applicable to the solution of this problem. The first of these involves substitution of much higher oxygen content binders for the polymeric fuel. In Figure 1 and Table I the results of substituting highly oxygenated polyester

polymers for the conventional fuel can be seen. Use of a carboxy-terminated polyester based on diethylene glycol and adipic acid, with an oxygen content of 37.0% results in almost a 50% reduction in solid carbon in the exhaust. The required amount of NH_4ClO_4 oxidizer for a 2200°F temperature is reduced to approximately 62%. For a 42.0% oxygen content binder, the amount of oxidizer for generation of 2200°F is reduced still further, to approximately 58%. Since one of the combustion products resulting from the use of NH_4ClO_4 is HCl, with its consequent erosivity of certain metals of construction, these reductions in oxidizer content are quite desirable, since they result in corresponding reductions in HCl content.

The second method of lowering flame temperature involves the addition of a third component to the system that is as low in energy content as possible and that has an internal oxidation ratio close to 1.0. Compounds with these high negative heats of formation and balanced stoichiometry are aptly designated as "coolants", since they are both poor fuels and poor oxidizers. A representative list of compounds of this type is shown in Table II. The oxidizers, ammonium perchlorate and ammonium nitrate, are included for comparison.

For each compound, the empirical formula, density, oxidation ratio, and heat of formation in kilocalories per gram are given. Because warm gas generating systems must be efficiently packaged, high density values are desirable. The advantage of possessing an oxidation ratio close to 1.0 has already been pointed out. Finally, since high flame temperatures result from either low negative or positive heats of formation, it is desirable that the value for $\Delta H_f/M$ be as large a negative number as possible, in order to produce low flame temperatures.

Examination of the compounds in Table II shows materials ranging from low oxidation ratio fuel-like compounds such as oxamide and azodicarbonamide, to more evenly balanced materials such as ammonium oxalate hydrate, oxalohydroxamic acid, and hydroxylammonium oxalate. Ammonium dihydrogen phosphate theoretically appears to be an oxidizer, like ammonium nitrate, and ammonium perchlorate; however, in actuality it serves only as a coolant, since the phosphate portion of the molecule is extremely stable at elevated temperatures, and is not a source of oxygen, unlike the nitrate and perchlorate structures.

As might be expected, the compounds in the middle of the list are the most desirable and useful coolants; in particular, oxalohydroxamic acid (also sometimes referred to as dihydroxyglyoxime-DHG) is of particular interest. Its high density, balanced stoichiometry and negative heat of formation are of importance in this regard.

Table III points out still another important factor in the selection of an effective coolant. A good coolant is thermally stable, but not too stable. Oxalohydroxamic acid is quite satisfactory in this respect, showing no endotherm or exotherm in differential thermal analysis below 300°F, but it completely fumes off at the slightly higher temperature of 338°F (dec.). Its ammonium salt, on the other hand, exhibits its first exotherm at a lower temperature than 300°F, but it is not completely decomposed until 400°F is reached. The other coolants shown are more stable in a thermal sense, but this frequently means that the amounts that can be added to a propellant formulation are limited to low levels because of difficulty in achieving combustion.

The effect of adding various amounts of coolant to typical warm gas generator propellant compositions is shown in Figure 2. At the same binder content of 26.5%, larger amounts of oxalohydroxamic acid (DHG) are required to reduce the flame temperature of the 43% oxygen content binder to the 2200°F level than for the 37% oxygen content binder. The more negative heat of formation of hydroxylammonium oxalate makes it possible to reach the 2200°F level with even less coolant. The

overall effectiveness of these coolants is realized when the flame temperatures of the same compositions without coolant are compared, for these are 4250°F and 3900°F, respectively, for the 42% and 37% oxygen binders. Hydroxylammonium oxalate (HAO) is especially effective in improving the cleanliness of the exhaust for only 22% of this coolant produces a 2278°F flame temperature with no solid carbon in the exhaust products.

In addition to the foregoing methods of reducing carbon in the exhaust products, it is also possible to effect a reduction by reducing the pressure at which the combustion reaction is carried out. An indication of the extent of this factor can be seen in Figure 3, where the weight percent of solid carbon formed in the Exhaust is plotted as a function of the combustion pressure for a single composition over the pressure range of 100 psia to 20,000 psia. At 20,000 psia, the carbon content of the exhaust is over 5% by weight, while at pressures below 500 psia, 0% carbon results. A reduction in flame temperature also results, with the value of 2374°F for the 20,000 psia level decreasing to 2058°F at 100 psia.

In addition to the formation of solid carbon, it is also possible for ammonium chloride to condense in solid crystalline particles during the reduction of flame temperature resulting from expansion of the combustion gases through a nozzle or turbine system. The presence of chlorine in the ammonium perchlorate leads to the formation of HCl as one of the combustion products; this in turn reacts with traces of NH_3 in the composition products to form NH_4Cl when the temperature of the system falls below the value at which the vapor pressure of NH_4Cl is equal to the pressure of the system. A plot of the vapor pressure - temperature relationship for NH_4Cl is shown in Figure 4. If the temperature and pressure of the system fall above the line, solid NH_4Cl will not form; when either the temperature or the pressure or both are reduced sufficiently to fall below the line, formation of solid particles will occur. In general, the higher the pressure in the system, the less likely it is that NH_4Cl will deposit on cold walls or surfaces in the system.

Another problem resulting from the presence of HCl in the combustion products is the reaction of small amounts of this acid with the metallic materials of construction in systems using warm gas generators of this type. The metal chlorides formed from these reactions are undesirable for two reasons: changes in the dimensions of the attacked metal surfaces result from a volatilization of the chlorides, and later on deposition of metal chloride particles can occur in unwanted locations as the temperature of the gas is reduced.

Table IV shows the deposition temperature (melting point) for several of these metallic chlorides at a pressure of 1000 psia (68.05 atmospheres). They are arranged in order of increasing volatility. Although the rate of erosion of surfaces of most of these metals is extremely slow, as shown by the data on loss rate, the amounts of the chlorides formed are still of concern in some applications. The use of carbon steel is undesirable, but some stainless steels are satisfactory due to the protective action of chromium and nickel. The use of molybdenum and its alloys results in good erosion resistance and volatile chlorides for the reaction products.

Finally, it should be pointed out that a general correlation exists for a great many of the specific compositions described in this paper between theoretical flame temperature and % solid carbon in the exhaust. This can be seen in Figure 5, for with a few exceptions, all of the compositions previously discussed fall within a single band. Above a flame temperature of approximately 2550°F, no carbon forms; while below this temperature the amount formed is inversely related to the temperature.

In summary, two general methods of obtaining low flame temperature propellant compositions have been described that do not result in the production of large (over 6%) quantities of solid carbon in exhaust products. These are the use of highly oxygenated polyester binders and the use of "coolant" compounds with large negative values of $\Delta H_f/M$ and oxidation ratios close to 1.0. Two useful compounds of this type are oxalohydroxamic acid and hydroxylammonium oxalate.

The effects of varying combustion pressure over the range of 100 to 20,000 psia have been described. Effects related to the presence of HCl in the system, including the conditions controlling solids such as NH_4Cl and various metallic chlorides in the system have also been discussed.

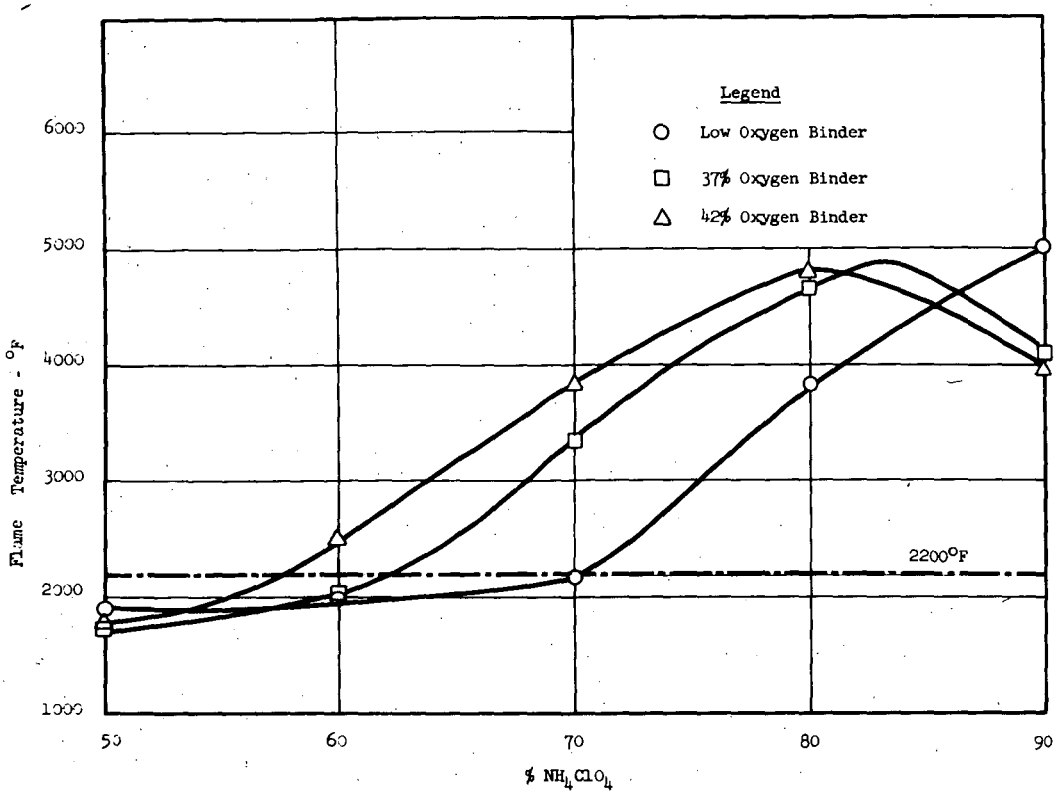


Figure 1. Effect of Oxygen Content on Flame Temperature

Table I

Reduction of Carbon Content
of
Combustion Products

Binder	Wgt. % Oxidizer/Coolant	Flame Temp. (^{o}F)	Oxidation Ratio	Wgt.% $C_{(s)}$ in Exhaust
Low Oxygen Content	70/0	2186	1.15	6.45
37% Oxygen Content	60/0	2028	1.56	3.52
37% Oxygen Content	43.5/30	2138	1.69	1.99
42% Oxygen Content	37.5/36	2175	1.74	1.88

Table II

Coolants

Compound	Empirical Formula	Density (g/cc)	Oxidation Ratio	$\frac{\Delta H_f}{M}\left(\frac{kcal}{g}\right)$
Azodicarbonamide	$C_2H_4O_2N_4$	1.68	0.5	-0.60
Oxamide	$C_2H_4O_2N_2$	1.667	0.5	-1.375
Ammonium Oxalate Hydrate	$C_2H_{10}O_5N_2$	1.50	0.715	-2.40
Oxalohydroxamic Acid	$C_2H_4O_4N_2$	1.85	1.0	-1.138
Hydroxylammonium Oxalate	$C_2H_8O_6N_2$	1.60	1.0	-1.85
Ammonium Dihydrogen Phosphate	$NH_4H_2PO_4$	1.803	1.33	-3.02
Ammonium Nitrate	NH_4NO_3	1.725	1.5	-1.09
Ammonium Perchlorate	NH_4ClO_4	1.95	2.0	-0.60

Table III

Differential Thermal Analysis

of Coolants

Coolant	Endotherm (°F)	Exotherm (°F)	Fumes (°F)
Oxalohydroxamic Acid	None	311.0	338.0
Ammonium Oxalohydroxamate	None	266.0	401.0
Hydroxylammonium Oxalate	271.4	348.8	399.2
Azo-dicarbonamide	None	372.2	451.4
Ammonium Oxalate Hydrate	192.2 + 413.6 (dec.)	None	None

Table IV

Formation and Deposition of Metallic Chlorides

Metal	Milligrams of Loss per 10 grams	Highest Melting Chloride	
		Chloride	Melting Point (°C)
Cr	0 (1)	$CrCl_3$	1150
Ni	---	$NiCl_2$	1001
Fe	3.6	$FeCl_2$	670-674
Ti	2.7	$TiCl_3$	dec. 440
Zr	---	$ZrCl_4$	437
W	---	WCl_6	275
Nb	0	$NbCl_5$	204.7
Mo	0	$MoCl_5$	194

(1) 304 Stainless Steel

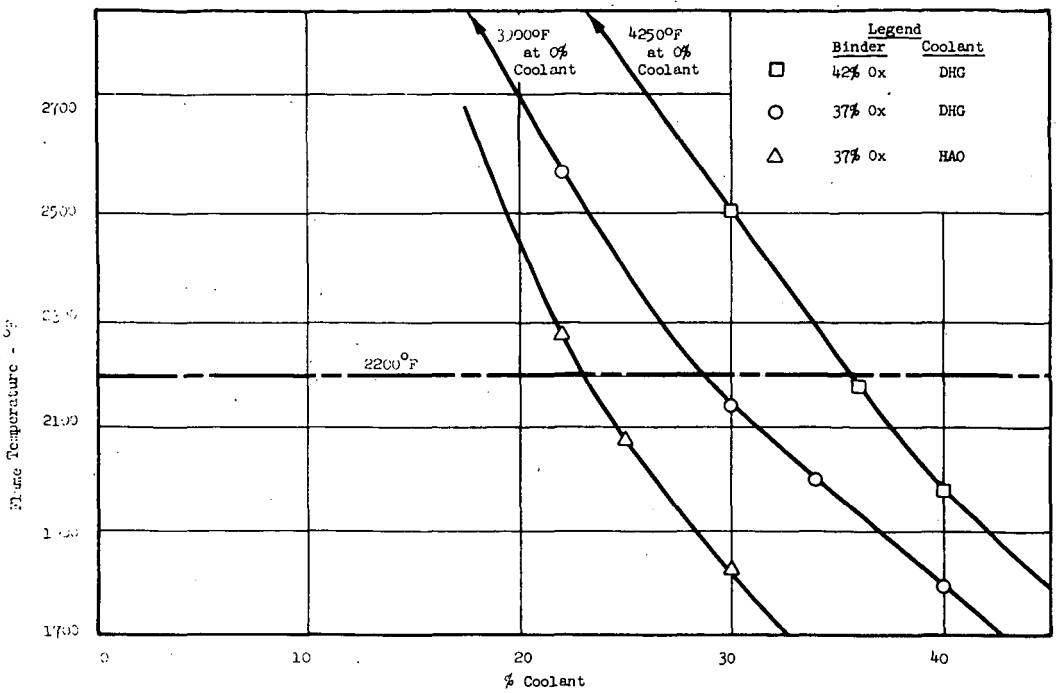


Figure 2. Effect of Percentage of Coolant on Flame Temperature

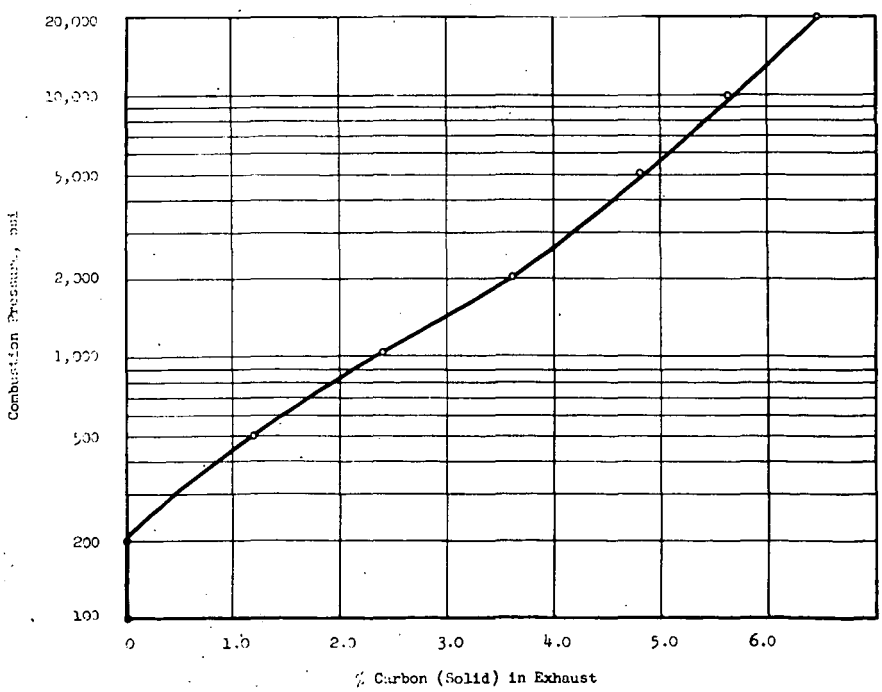


Figure 3. Effect of Pressure on % Carbon(s)

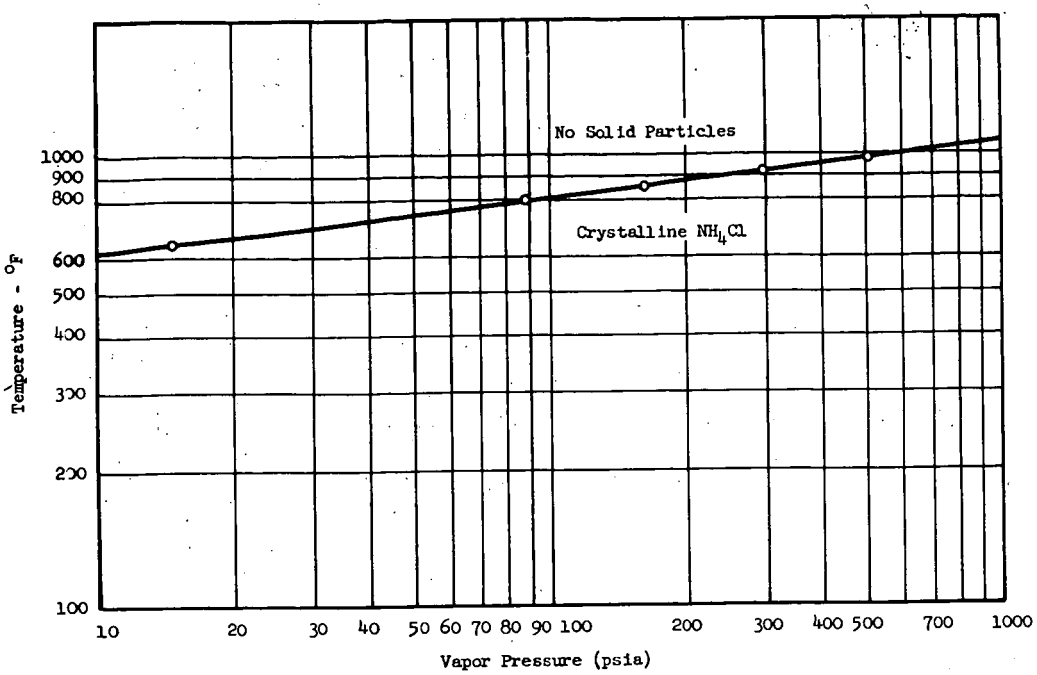


Figure 4. Vapor Pressure of NH_4Cl

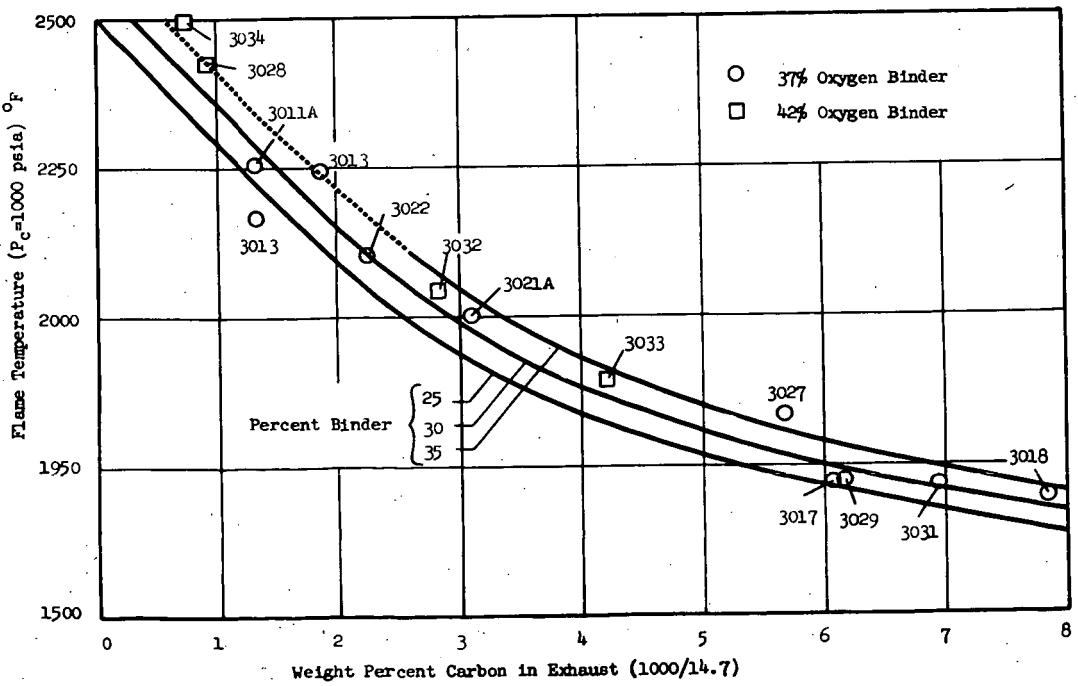


Figure 5. Temperature vs. Carbon Content of Q Series DHC-AP Propellant Compositions

THE SYNTHESIS OF FLUORAMMONIUM SALTS[1]

Vytautas Grakauskas, Allen H. Remanick, and Kurt Baum

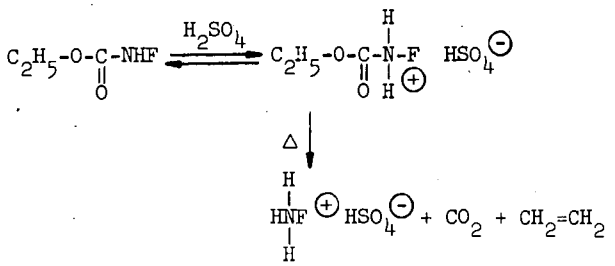
Contribution from Chemical & Biological Processes,
Aerojet-General Corporation, Azusa, California 91703.

Of the four possible fluorine-substituted ammonium ions, only the tetrafluoro derivative has been reported as a stable salt.[2,3] Difluoramine and trifluoramine have been reported to form reversible complexes with Lewis acids at low temperatures. Fluoramine was claimed to be a by-product of the electrolysis of ammonium bifluoride[5,6] but the results have been shown to be in error.[7] Dimethylfluoramine was synthesized by the fluorination of unsymmetrical dimethylsulfamide and the compound was sufficiently basic to form a stable hydrochloride.[8] Fluorimonium salts prepared by the rearrangement of alkyldifluoramines[9] can also be considered as alkylidene derivatives of substituted fluoramines.

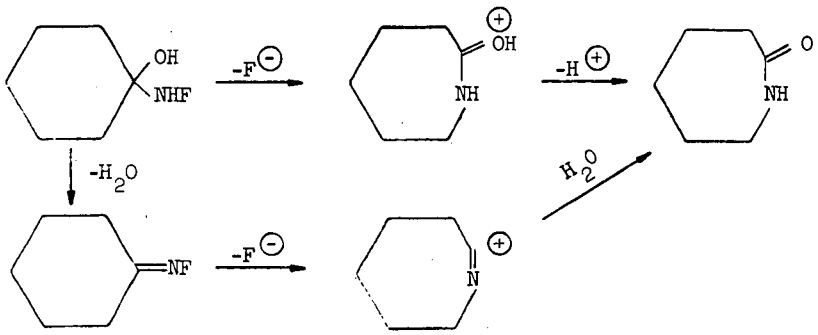
Simple salts of fluoramine have now been prepared by the reaction of alkyl N-fluorocarbamates with strong acids. The starting materials are synthesized readily by the fluorination of alkyl carbamates.[10]

Fluorammonium Bisulfate. Fluorimonium salts have been prepared and characterized in sulfuric acid. Under these conditions, the hydrolysis of N-fluorocarbamates in sulfuric acid would be expected to give the fluorammonium ion, which also should be stable.

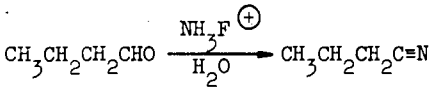
When a solution of ethyl N-fluorocarbamate in concentrated sulfuric acid was heated at 85 to 90°, carbon dioxide and ethylene were evolved. The F^{19} nmr spectrum of the sulfuric acid solution consisted of a quartet at 36.8 ppm relative to external trifluoroacetic acid, with a coupling constant of 38 cps. Thus, the fluorine was coupled to three equivalent hydrogens, and it is noteworthy that the hydrogens did not exchange rapidly with the solvent. By contrast, the F^{19} spectrum of an unheated solution of ethyl N-fluorocarbamate in sulfuric acid consisted of a single broadened signal at 27.5 ppm; the NH protons of the starting material thus exchanged with the solvent rapidly by the nmr time scale.



Additional evidence for the fluorammonium ion structure was obtained from reactions with carbonyl compounds. The reaction of cyclohexanone with a sulfuric acid solution of fluorammonium bisulfate gave ϵ-caprolactam, isolated by quenching the mixture with ice. A probable intermediate was α-fluoraminocyclohexanol, which could lose a fluoride ion and undergo nucleophic ring expansion. Alternatively, the dehydration of this alcohol could give fluoriminocyclohexane, which in turn, would undergo a similar ring expansion. The Beckmann fragmentation of fluorimines has been reported recently.[11]



When n-butyraldehyde was treated similarly with the fluorammonium bisulfate solution, n-butyronitrile was formed. A related reaction, carried out in the presence of base instead of acid is the synthesis of nitriles from aromatic aldehydes and chloramine.[12]



Attempts to isolate pure fluorammonium bisulfate, by diluting the sulfuric acid solution with organic solvents, were unsuccessful.

Fluorammonium Perchlorate. Perchloric acid, which is more volatile than sulfuric acid, appeared to offer better possibilities for the isolation of a pure fluorammonium salt. Accordingly, a solution of ethyl N-fluorocarbamate in 70% perchloric acid was heated until gas was evolved (68°), and the excess perchloric acid was then removed under vacuum. However, the product was contaminated by organic material of low volatility. Isopropyl N-fluorocarbamate reacted with 70% perchloric acid at a lower temperature than the ethyl ester (35 to 40°), and gave a less contaminated, but still unsatisfactory product. Unexpectedly, fluorammonium perchlorate was found to have appreciable vapor pressure, subliming slowly at 46°/.02 mm; the sublimed salt was analytically pure.

It is well-recognized that the maximum acid strength of a solution is limited by the acidity of the conjugate acid of the solvent. For this reason, perchloric acid is a stronger acid in acetic acid that in aqueous solution.[13] Perchloric acid is soluble in chloroform[14]; therefore, this solvent, which has very low basicity, should enhance the acidity. Indeed, isopropyl N-fluorocarbamate reacted more rapidly with a 10% solution of anhydrous perchloric acid in chloroform, than with the 70% commercial reagent. An additional advantage was that fluorammonium perchlorate was insoluble in chloroform. Analytically pure product was isolated directly in quantitative yield. The fate of the isopropyl group was not determined, but inasmuch as carbon dioxide free of propylene was liberated, it appears likely that isopropyl perchlorate was formed; if it was formed, it would remain in solution.[15]

$$(CH_3)_2CHOCNHF + 2\ HClO_4 \xrightarrow[42\text{-}43^\circ]{CHCl_3} (CH_3)_2CHOClO_3 + CO_2\uparrow + \underline{NH_3FClO_4}$$

Fluorammonium perchlorate was a white solid which melted with decomposition at 104 to 105°. Differential thermal analysis showed a sharp exotherm at this temperature. The impact sensitivity was the same as that of RDX. The salt was hygroscopic and decomposed rapidly in the presence of atmospheric moisture. Although the synthesis and isolation was carried out in glass equipment under an atmosphere of dry nitrogen, some etching of the glass was visible after several hours of contact with the salt. However, samples have been stored at room temperature for several months, without decomposition, in fluorocarbon or passivated-nickel containers.

Fluorammonium perchlorate was insoluble in hydrocarbons and halocarbons; it was soluble in simple esters, nitriles, nitroalkanes, and in such ethers as monoglyme and tetrahydrofuran. It formed a 1:1 complex with dioxane. Concentrated solutions (e.g., 30 to 50%) in any solvents were unstable, and in several instances, fumed off shortly after they were prepared. Addition of chloroform to the ethyl acetate solution precipitated unchanged fluorammonium perchlorate.

The fluorine nmr spectrum of fluorammonium perchlorate in sulfuric acid consisted of a quartet (J = 44.1 cps) at 34.3 ppm from trifluoracetic acid (ϕ = 110.8), while the proton spectrum showed a doublet (J = 44 cps) at 10.28 δ.[16] However, when acetonitrile was used as the nmr solvent, the proton spectrum gave a broadened singlet at 10.7 δ, while the fluorine spectrum gave a slightly unsymmetrical singlet at 122.4 ϕ. In ethyl acetate, the proton signal was a sharp singlet at 11.5 δ, and the fluorine signal was a sharp singlet at 122.8 ϕ. Thus, rapid hydrogen exchange took place in the organic solvents but not in sulfuric acid. If the mechanism of exchange were direct displacement of protons, a higher rate could be expected in sulfuric acid than in the organic solvents. The more basic solvents apparently allow dissociation of fluorammonium perchlorate, to a small extent, to fluoramine and perchloric acid. The high volatility of fluorammonium perchlorate, compared to that of ammonium perchlorate might also be the result of dissociation.

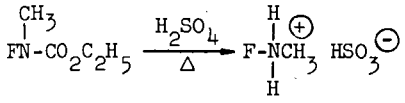
$$H_3\overset{\oplus}{N}F\ ClO_4^{\ominus} \rightleftharpoons H_2NF + HClO_4$$

Fluorammonium Methanesulfonate - Fluorammonium methanesulfonate was synthesized by heating ethyl N-fluorocarbamate and methanesulfonic acid at 90°. The salt was precipitated by the addition of ether. The melting point and dta exotherm were essentially the same as those of the perchlorate, and of the perchlorate-dioxane complex; this temperature range appears to be the stability limit of the fluorammonium ion.

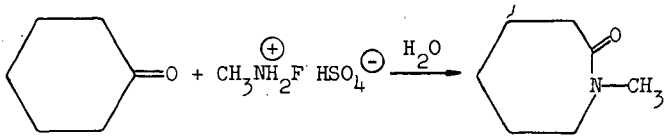
$$(CH_3)_2CHOCNHF + CH_3SO_3H \longrightarrow H_3NF \oplus CH_3SO_3^{\ominus}$$

The infrared spectrum is described in the Experimental Section.

Methylfluorammonium Bisulfate - To determine whether substituted fluorammonium salts could be prepared by these methods, the reaction of ethyl N-fluoro-N-methylcarbamate with sulfuric acid was studied. Gas was evolved at 85 to 95°. The F^{19} nmr spectrum of the sulfuric acid solution consisted of an incompletely resolved triplet of quartets at -29.5 ppm (external trifluoroacetic acid reference), with coupling constants of 42 cps to the NH_2 and 28 cps to the methyl.



A sulfuric acid solution prepared in this manner reacted with cyclohexanone and water to give N-methylcaprolactam.



These reactions are analogous to those of the unsubstituted fluorocarbamates and indicate broad applicability of the synthesis methods.

Acknowledgement. The authors wish to thank Dr. H. M. Nelson and Mr. L. A. Maucieri for the nmr spectra, and Mr. K. Inouye for the elemental analysis.

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16. One member of the doublet was obscured by the solvent signal in concentrated sulfuric acid, but was visible using 101% sulfuric acid.

PREPARATION AND POLYMERIZATION OF NF_2-CONTAINING MONOMERS

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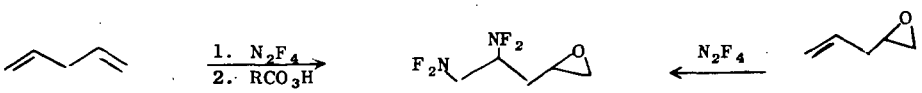
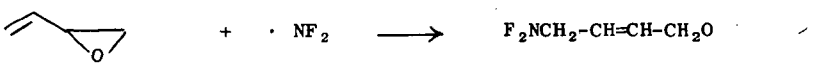
Polymeric compositions normally employed to hold the oxidizer and fuel components of solid rocket propellant system do not contribute to the energetics of the propellant. In advanced solid propellants use of non-energetic binders is particularly deleterious to the attainment of high Isp. Preparation of binders containing the energetic difluoramino group was studied. Introduction of this group into polymer monomers was realized by the free radical addition of N_2F_4 to olefins. The difluoramino oxiranes synthesized for this work were obtained by either of the illustrated routes.



Attempts to difluoraminate vinyl oxiranes in which the vinyl function is directly attached to the ring were unsuccessful. These systems yield free radical induced rearrangements involving the olefinic and the oxirane functions.



These rearrangements will be discussed. Difluoramination of 3-methylene oxetane yielded a mixture of the expected product together with a difluoramino aldehyde. Polymerization of the NF_2-oxiranes and oxetane will be described.

KINETICS OF THE GAS PHASE PYROLYSIS OF CHLORINE PENTAFLUORIDE[1]

by A. E. Axworthy and J. M. Sullivan

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The kinetics of the photochemical formation of chlorine pentafluoride from ClF_3 and F_2 has been studied recently by Krieger, Gatti, and Schumacker.[2] We report herein the results of our investigation of the gas phase thermal decomposition of ClF_5.

EXPERIMENTAL

The electrically-heated stirred flow reactor (91-ml, monel) employed is described elsewhere.[3,4] Chlorine pentafluoride vapor of 98 weight percent purity (containing about 1.3% HF and 0.7% ClF_3) was passed through the reactor at an initial partial pressure of 32 mm in a mixture with helium. The total pressure was 1 atm. The reactor was equipped with a by-pass to allow measurement of the ClF_5 concentration in the entering gas stream.

The gases leaving the reactor (or the by-pass) were passed through a 10-cm nickel infrared cell with AgCl windows. The ClF_5 concentration was followed by measuring the absorbance at 12.5 microns. The flow rates were measured with a soap bubble flow meter connected to the exit stream. The measured flow rates and reactor volume were corrected to reactor temperature. No correction was made for the partial dissolution of reactants and products in the soap solution or for the presence of water vapor.

Infrared analysis of the exit gas showed ClF_3 and ClF_5 as the major absorbers, with ClF present in trace quantities. Fluorine does not absorb in this range (2-15 microns). These results indicate that the stoichiometry is mainly:

$$ClF_5 \rightarrow ClF_3 + F_2 \qquad \Delta H = +18.5 \text{ kcal/mole}^5 \tag{1}$$

RESULTS

The results obtained for the thermal decomposition of ClF_5 over the temperature range 252-307° are presented in Table 1. For a stirred flow reactor, the rate constants for a simple order, single-reactant reaction are given by the equation:

$$k_n = (P^\circ - P)/(P^n\tau) \tag{2}$$

where P° and P are the partial pressures, respectively, of reactant entering and

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1. This work was supported by the United States Air Force under Contract No. AFO4(611)-10544.
2. R. L. Krieger, R. Gatti, and H. J. Schumacker, Z. Phys. Chem., 51, 240 (1966).
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5. JANAF Thermochemical Tables, Quarterly Supplement No. 7.

leaving the reactor, τ is the average residence time in the reactor, and n is the order of the reaction.[4] It can be shown from eq 2 that for a first-order reaction, a plot of $\alpha/(1-\alpha)$ vs τ, where α is the fraction reacted, should be linear with a slope equal to the rate constant. Figure 1 shows that the decomposition of ClF_5 follows first-order kinetics up to 80% reaction at 293°. The data in Figure 1 were obtained at temperatures of 291.5-294.0°, and corrected to 293.0° using an activation energy of 41 kcal/mole. The rate constant, k_1, from each experiment is listed in Table 1. The best first-order rate constant, k_1^A, at each temperature, obtained from a plot of the type shown in Figure 1, is given in the last column of Table 1 and plotted in the Arrhenius form in Figure 2. A least squares fit of the data to the Arrhenius expression yields the line shown in Figure 2 which represents the rate expression:

$$k_1 = 10^{14.61} \exp(-41{,}330/RT) \text{ sec}^{-1} \qquad (3)$$

The uncertainty in activation energy is about 2 kcal/mole.

The mixing requirements for a stirred flow reactor do not allow a convenient procedure for varying widely the surface-to-volume ratio, but the high values of the activation energy and preexponential factor suggest that the reaction is homogeneous in nature. Also, it was found that the rates were unchanged after the reactor, containing products of reaction, had been allowed to sit at 280° for 1 month.

DISCUSSION

Three possible mechanisms may be written which are compatible with the observed rate expression, i.e., first order in ClF_5 with no apparent inhibition as the products accumulate:

A) Unimolecular Elimination of F_2

$$ClF_5 \rightarrow ClF_3 + F_2 \qquad (4)$$

B) Non Chain Radical Mechanism

$$ClF_5 \rightarrow ClF_4 + F \qquad (5)$$
$$ClF_4 \rightarrow ClF_3 + F \qquad (7)$$
$$F + F + M \rightarrow F_2 + M \qquad (9)$$

C) Long Chain Radical Mechanism

$$ClF_5 \rightarrow ClF_4 + F \qquad (5)$$
$$F + ClF_5 \rightarrow ClF_4 + F_2 \qquad (6)$$
$$ClF_4 \rightarrow ClF_3 + F \qquad (7)$$
$$F + ClF_4 \rightarrow ClF_3 + F_2 \qquad (8)$$

The long chain mechanism (C) may be questioned on the basis of the observed rate parameters A and E. Mechanism (C) requires that

$$A = \left(\frac{A_5 A_6 A_7}{A_8}\right)^{\frac{1}{2}} \quad \text{and} \quad E = \tfrac{1}{2}\left(E_5 + E_6 + E_7 - E_8\right)$$

The A factors for the individual steps can be estimated from the generalizations proposed by Benson and Demore[6]. Thus,

6. S. W. Benson and W. B. Demore, Ann. Rev. Phys. Chem., 16,426 (1965).

$\left(\frac{A_5 A_6 A_7}{A_8}\right)^{\frac{1}{2}} \sim \left(\frac{10^{14}\ 10^{14}\ 10^{10}}{10^{10}}\right)^{\frac{1}{2}} \sim 10^{14}$. This value is in good agreement with the observed value of $10^{14.6}$. $E_5 + E_7$ are assumed equal to $\Delta H^\circ + E_{-7}$, where ΔH° is the heat of reaction for $ClF_5 \rightarrow ClF_3 + 2F$ (ΔH° = 57 KCal/mole)[4] and E_{-7} is the activation energy for the reverse of reaction (7). Semenov's approximation[7] gives E_{-7} = 2.5 KCal/mole and E_6 = 11.0 KCal/mole. The radical-radical reactions (-5) and (8) are assumed to have zero activation energies. Therefore $E = \frac{1}{2}(57.0 + 2.5 + 11.0\text{-}0) \sim 35$ KCal/mole. This value is somewhat lower than the observed value of 40.3 KCal/mole and suggests that the long chain mechanism (C) probably is not important in the decomposition of ClF_5.

Unfortunately the data do not allow a choice to be made between the molecular elimination mechanism (A) and the non chain mechanism (B). Thermochemical data[5] give $K_{eq} = 10^{-8.85} 10^{\frac{18.5}{\theta}}$ for the reverse of reaction (4). Therefore, $k_{-4} = 10^{5.8} \exp(-22{,}800/RT)$ liter/mole sec. The A factor $10^{5.8}$ liter/mole sec is not unreasonable for a bimolecular reaction. Hence, the molecular elimination reaction (A) cannot be eliminated.

If the non chain radical mechanism (B) is correct, then the measured activation energy, 40.3 KCal/mole, is equal to the bond dissociation energy for the first Cl-F bond in ClF_5. This value seems reasonable since the average bond energy in ClF_5 is 36 KCal/mole[5]. Further support for the non chain radical mechanism is given by the generalization of Benson and DeMore[6] that the A factor of unimolecular reactions involving the splitting off of atoms are in the range of 10^{14} to 10^{15} sec^{-1}.

It now remains to discuss the recent photochemical investigation by Krieger et al.[2] They studied the kinetics of the photochemical formation of ClF_5 from ClF_3 and F_2 (365 mμ, 16-70°) and obtained the complex rate expression:

$$\frac{d(ClF_5)}{dT} = kI_a \left[\frac{k'(ClF_3)}{M} + 1 + \frac{k''}{M}\right]^{-1}$$

Their somewhat unusual mechanism involves the formation of an activated ClF_5 molecule which can (1) be collisionally deactivated to ClF_5, (2) react directly with ClF_3 to form 2 ClF_4 radicals, or (3) split into ClF_4 + F. In order to explain their observed results (quantum yield dependent on inert gas pressure and on ClF_3 pressure), all three of these processes must occur to an appreciable extent in each of their experiments.

These photochemical results indicate that the ClF_5 activated molecule decomposes more rapidly than classical theory would predict. Also, the thermal decomposition of ClF_5 should be pressure dependent and accelerated by the presence of the product ClF_3.

The thermal and photochemical results can be shown to be compatible in two ways. First, it can be calculated from the photochemical rate constants that the accelerating effect of ClF_3 would not be sufficient to appreciably affect the first-order plot shown in Fig. 1. Thermal experiments would have to be run with added ClF_3 and at various total pressures to determine if the decomposition is dependent on the

7. N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Volume I, Princeton University Press, Princeton, New Jersey, 1958, P 29.

concentration of ClF_3 and added inert gases.

If it turns out that the thermal decomposition rate is unaffected by added ClF_3 and inert gases, it could be argued that the activated complex in the photochemical reaction differs in average energy from the thermally-formed activated complex. The fluorine atoms formed in the photochemical decomposition of F_2 must contain considerable translational energy since there are no accessible electronic states. If a portion of this translational energy is converted to internal energy in the ClF_5 complex ($F + ClF_4 \rightarrow ClF_5^*$), the stability of the complex would be greatly reduced. For example, an additional 10 KCal/mole of activation energy would decrease the predicted half-life of the complex from about 10^{-8} to about 10^{-10} sec, and might also account for its reactivity toward ClF_3.

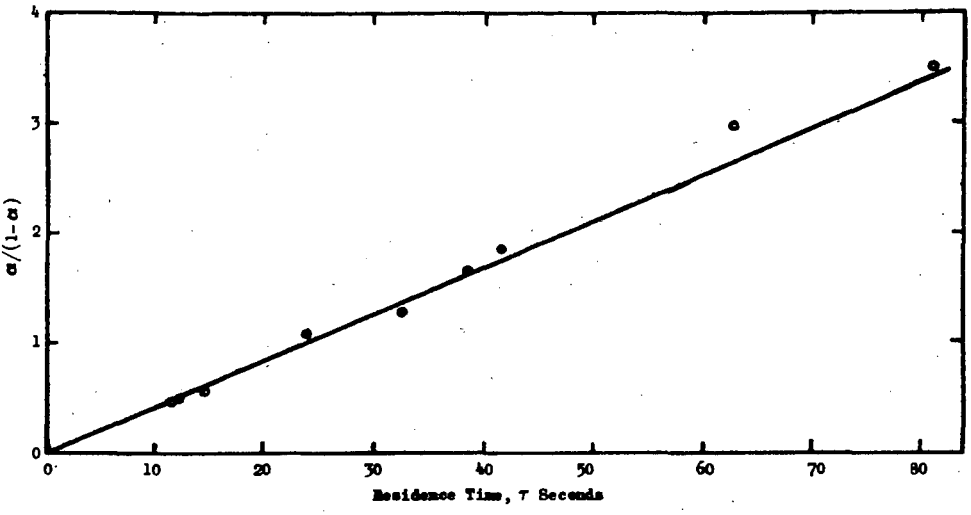

Figure 1. First-Order Plot of ClF_5 Decomposition Data at 293 C

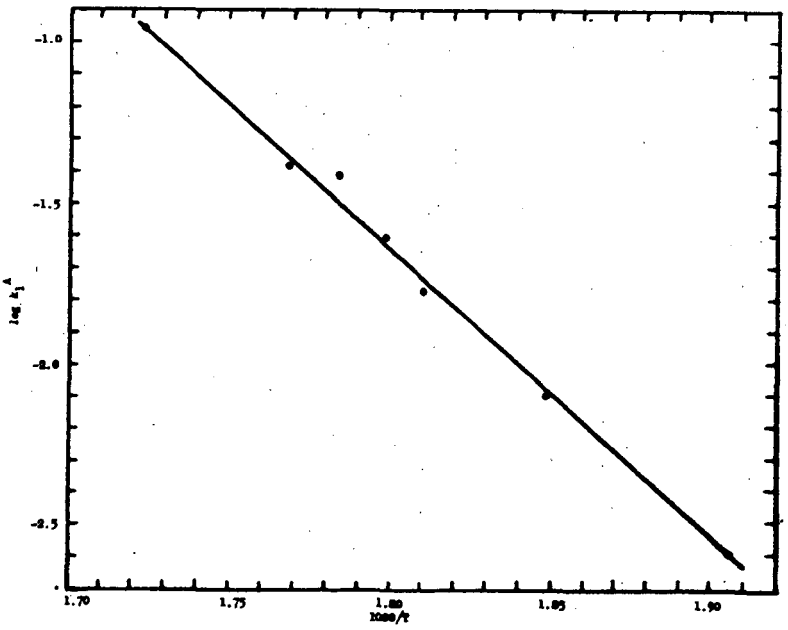

Figure 2. Arrhenius Plot

Table 1. Experimental Kinetic Data for the Pyrolysis of Gaseous Chlorine Pentafluoride

Temp, °C	τ, sec	Fraction Reacted, α	k_1, sec^{-1}	k_1^A, sec^{-1}
252.2	24.9	0.068	0.00292	0.00260
252.2	113.0	0.254	0.00300	
252.2	281.5	0.375	0.00213	
252.2	449.0	0.525	0.00246	
268.5	196.8	0.612	0.00803	0.00803
279.4	36.2	0.381	0.0170	0.0164
279.4	115.3	0.646	0.0158	
283.2	23.6	0.371	0.0250	0.0251
283.0	36.3	0.477	0.0252	
287.4	24.4	0.465	0.0357	0.0385
288.2	40.4	0.625	0.0413	
287.4	42.4	0.629	0.0398	
287.6	55.0	0.716	0.0459	
291.8	11.9	0.312	0.0380	0.0417
291.5	24.1	0.499	0.0413	
293.0	11.6	0.312	0.0391	
293.0	14.6	0.364	0.0394	
293.3	32.4	0.570	0.0408	
293.0	38.4	0.624	0.0432	
293.5	41.7	0.658	0.0462	
293.0	62.8	0.749	0.0476	
294.0	81.3	0.790	0.0464	
307.5	7.96	0.433	0.0959	0.113
306.8	9.76	0.529	0.115	
307.0	11.93	0.595	0.123	
307.5	12.9	0.583	0.109	

Redox in the Cl_2O–AsF_5 System

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Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF_5 at -78° and at about -50° formed an odd molecule, $ClOAsF_5$, through elimination of Cl_2.[1] Inference of the structure as being the postulated odd molecule was drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO_2 to give $ClNO_3$.

We were interested in studying various aspects of the proposed odd molecule particularly as a ready source of the ClO radical. However, we felt that, prior to utilizing $ClOAsF_5$ as an intermediate, a more complete characterization was in order.

Experimental

Materials. Chlorine monoxide was prepared from Cl_2 and yellow HgO using a modified procedure.[2] Arsenic pentafluoride was purchased from Ozark-Mahoning and used without purification after gas chromatography indicated a purity of better than 99.5%. Chloryl fluoride was prepared from $KClO_3$ and F_2[3] and purified by fractional condensation. Nitrogen tetroxide was purchased from the Matheson Co. and purified by fractional condensation. Phosphorus dichloride trifluoride was formed[4] from PF_3 and Cl_2.

Apparatus. Experiments were conducted in two vacuum systems, one constructed of glass, the other of stainless steel-Teflon. Solids were handled in an inert atmosphere glove box. Infrared spectra were taken on a Perkin-Elmer 137 Infracord using 5-cm gas cells fitted with AgCl windows or halocarbon oil mulls between AgCl plates. Debye-Scherrer powder X-ray diffraction patterns were obtained with a G. E. XRD5 instrument using $CuK\alpha$ radiation.

Vapor phase chromatography of reactants and products was carried out on a column packed with 50% w/w of Halocarbon Oil 4-11V and Kel-F low density molding powder according to Dayan and Neale.[5]

(1) M. Schmeisser, W. Fink and K. Brandle, Angew. Chem. 69, 780 (1957).

(2) C. J. Schack and C. B. Lindahl, Inorg. and Nucl. Chem. Letters, 3, 387 (1967).

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Reactions of Cl_2O and AsF_5. Measured quantities of Cl_2O (117 cc, 5.22 mmoles) and AsF_5 (85.0 cc, 3.79 mmoles) were separately condensed into the reactor (glass or Teflon tubes) at -196°. The temperature was changed to -78° and it was observed that the mixed reactants gradually developed a dark red color. Pumping on the mixture after a few hours at -78° resulted in the recovery of some of the starting materials and much Cl_2. Subsequent warming of the reaction to ambient temperature gave additional small amounts of gaseous materials and a white solid. Little or no -196° non-condensable gases were observed throughout the reaction. In all, 111 cc of volatile products were obtained. Infrared and gas chromatographic analysis indicated these products to be a mixture of AsF_5 (17.5 cc, 0.78 mmole) and Cl_2 (93.5 cc, 4.17 mmoles) with a trace of ClO_2 and no Cl_2O. The observed reactant-product ratio of Cl_2O:AsF_5:Cl_2 was 5.00:2.89:4.01. Similar reaction ratios were obtained when Cl_2O was used as the excess reagent. The solid product showed two infrared bands 1280 cm^{-1} (m, doublet) and 690 to 700 cm^{-1} (s. broad). Based on the observed stoichiometry of the reaction and the known infrared frequencies of Cl-O[6] and AsF[7] compounds, it appeared the solid might be principally ClO_2AsF_6. Accordingly, an authentic sample was prepared.

Preparation of ClO_2AsF_6. Chloryl fluoride (111 cc, 4.96 mmoles) and AsF_5 (63.7 cc, 2.84 mmoles) were separately condensed into a Teflon ampoule at -196°. After 1 hour at room temperature, the unreacted gases were removed and measured (48.0 cc, 2.14 mmoles). An infrared spectrum showed only $FClO_2$. The white solid product had an infrared spectrum identical to that of the solid from the Cl_2O-AsF_5 reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table 1.

Reaction of ClO_2AsF_6 and NO_2. Weighed amounts of ClO_2AsF_6 and excess NO_2 gas were reacted for 1 hour at 0°. The expected displacement[8] of ClO_2 was achieved but in poor yield; 20% for the solid from the Cl_2O reaction and 35% for the solid from the $FClO_2$ reaction.

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(5) V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p. 223.
(6) E. A. Robinson, Can. J. Chem., 41, 3021 (1963).
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(8) M. Schmeisser and W. Fink, Angew. Chem., 69, 780 (1957).

TABLE 1

X-RAY POWDER DIFFRACTION DATA FOR ClO_2AsF_6

d, Å	Relative Intensity	d, Å	Relative Intensity
7.50	30	2.30	10
5.55	30	2.08	60
5.10	30	2.05	60
4.40	70	1.95	40
4.02	40	1.87	10
3.65	100	1.84	10
3.57	90	1.80	10
3.49	10	1.76	10
3.03	50	1.70	20
2.87	≤ 10	1.59	15
2.76	≤ 10	1.55	10
2.69	≤ 10	1.53	10
2.54	≤ 10		

Reaction of PF_3Cl_2 and Cl_2O. A 1:1 mixture of PF_3Cl_2 and Cl_2O was allowed to warm to room temperature at which point an infrared spectrum was taken. The only infrared absorbing material present was POF_3. None of the PF_3Cl_2, a strong infrared absorber, remained. The by-product Cl_2 was revealed by its color when frozen. No non-volatile solids were observed.

Results and Discussion

The reaction of Cl_2O with AsF_5 does not give the odd molecule $ClOAsF_5$ but gives instead the salt ClO_2AsF_6. Further, the reaction appears to follow the stoichiometry shown in equation 1:

$$5Cl_2O + 3AsF_5 \longrightarrow 2ClO_2AsF_6 + 4Cl_2 + AsOF_3 \qquad (1)$$

The reaction stoichiometry does not appear to be dependent on the experimental reactant ratios. The formation of ClO_2AsF_6 was confirmed by preparing an authentic sample and comparing their X-ray patterns.

$$FClO_2 + AsF_5 \longrightarrow ClO_2AsF_6 \qquad (2)$$

In the reaction of Cl_2O with AsF_5, the evolution of Cl_2 apparently involves a much more complex process than a simple Cl-O bond rupture. The equation reported[1] for this process at -50° is shown in equation 3:

$$Cl_2O{\cdot}AsF_5 \longrightarrow ClOAsF_5 + 1/2\ Cl_2 \qquad (3)$$

We would prefer to propose an initial step that infers an ionization of Cl_2O, i.e., an ionic complex is obtained, perhaps $ClO^+AsF_5Cl^-$:

$$Cl_2O + AsF_5 \longrightarrow ClOAsF_5Cl \qquad (4)$$

The oxidation of the ClO^+ species could then proceed with additional Cl_2O:

$$Cl_2O + ClOAsF_5Cl \longrightarrow ClO_2AsF_5Cl + Cl_2 \qquad (5)$$

This step (equation 4) should not be considered unusual inasmuch as other chlorine oxides are capable of redox (e.g., ClO_2 gives some Cl_2O_6 on photolysis[9]).

The most difficult rationale is the formation of the AsF_6^- in the reaction. Admittedly a multiplicity of diverse reaction sequences could be proposed most of which would be difficult to experimentally verify. One possible path offered involves the dissociation of ClO_2AsF_5Cl into its components with the subsequent reactions noted:

$$ClO_2AsF_5Cl \longrightarrow FClO_2 + AsF_4Cl \quad (6)$$

$$2AsF_4Cl \longrightarrow AsF_3Cl_2 + AsF_5 \quad (7)$$

$$AsF_5 + FClO_2 \longrightarrow ClO_2AsF_6 \quad (8)$$

$$AsF_3Cl_2 + Cl_2O \longrightarrow AsF_3O + 2Cl_2 \quad (9)$$

It is readily seen that the sum of equations 4 through 9, suitably weighted, gives equation 1.

The identity of $AsOF_3$ was not established as a product since it is a non-volatile[10] X-ray amorphous solid. In addition, we did not wish to further complicate matters by studying the reaction of AsF_3Cl_2 with Cl_2O as a test of equation 8 inasmuch as AsF_3Cl_2 "goes ionic" and is formulated as $AsCl_4^+AsF_6^-$[11]. We did feel, however, that a suitable test of equation 8 would be the reaction of PF_3Cl_2 and Cl_2O. Indeed, the rapid conversion of PF_3Cl_2 to POF_3 and Cl_2 as in equation 10:

$$PF_3Cl_2 + Cl_2O \longrightarrow POF_3 + 2Cl_2 \quad (10)$$

strongly suggests that "covalent" AF_3Cl_2 would react similarly. The reaction conditions are such that the reorganization of AsF_4Cl, postulated as an intermediate in equation 6, would give initially the covalent structure.

The initial report on the preparations of "$ClOAsF_5$" did offer the reaction of NO_2 as a proof of the radical present[11]:

$$ClOAsF_5 + 2NO_2 \longrightarrow NO_2AsF_5 + ClNO_3 \quad (11)$$

The existence of NO_2AsF_5 has already been questioned seriously and apparently disproved[12]. Further, the formation of some $ClNO_3$ should be expected from ClO_2AsF_6 and NO_2 inasmuch as the reaction of ClO_2 and NO_2 gives $ClNO_3$[13]. It is quite likely that the reaction observed by Schmeisser et al.

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was the initial displacement of ClO_2 from ClO_2AsF_6 by NO_2 followed by a reaction of ClO_2 with NO_2, the overall reaction being:

$$ClO_2AsF_6 + 2NO_2 \longrightarrow NO_2AsF_6 + ClNO_3 + 1/2\ O_2 \qquad (12)$$

Except for the formation of the oxygen, the reaction in equation 12 has the same stoichiometry of NO_2 to "solid" as that reported in equation 11. Thus, the proof of "$ClOAsF_5$" through its reactions or its synthesis is not conclusive.

DENSITY, VISCOSITY AND SURFACE TENSION OF O_3-OF_2

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FREEZING POINT DEPRESSION IN LF_2 SYSTEMS

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INTRODUCTION

In some test programs at Douglas using liquid fluorine and liquid hydrogen, we found it was desirable to lower the freezing point of fluorine without appreciably affecting its chemical reactivity. The use of a eutectic mixture with another cryogenic oxidizer seemed the method of choice, and consideration of physical and chemical properties led us to select oxygen difluoride, OF_2, for the other component. Oxygen was also suggested, but was not used because of reports of the quenching effect oxygen has on the fluorine-hydrogen reaction (Reference 1), an effect we also found in our research on the ignition of the LF_2-LH_2 reaction in LH_2 (Reference 2) and which has also been reported in the OF_2-H_2 reaction (Reference 3). LO_2 was therefore dropped from further consideration.

Theoretical calculations of the freezing point depression in the F_2-OF_2 system were carried out. These suggested that experimental investigation was warranted.

THEORETICAL

The equilibrium or phase diagram of a two-component solid-liquid system may assume several general forms according to the nature of the components (Reference 4); these forms may be classified as follows:

1. Eutectic Systems
   - a. Simple eutectic
   - b. Monotectic (special form of simple eutectic)
   - c. Compound formation with congruent melting point
   - d. Compound formation with incongruent melting point
2. Completely Miscible Solid Solutions
   - a. Continuous solid solution
   - b. Minimum melting solid solution
   - c. Maximum melting solid solution
3. Partially Miscible Solid Solutions
   - a. Peritectic solid solution
   - b. Eutectic solid solution

In order for nonpolar compounds to form solid solutions, the following conditions must generally be satisfied:

1. Analogous chemical constitutions
2. Similar crystal structures
3. Nearly equal molecular volumes

While little is known of the crystal structures of F_2 and OF_2, it is certain that conditions 1 and 3 are not satisfied, and it is unlikely that solid solutions will form. Furthermore, there is no known tendency toward compound formation between OF_2 and F_2. Thus simple eutectic or monotectic systems are probable -- and the latter are rarely encountered.

If it is assumed that the system would be a simple eutectic, with the solution of each component in the other obeying Raoult's Law, and the liquidus curves conforming to equations for ideal solutions, the following considerations will apply:

From the Clausius-Clapeyron equation it can be shown that for equilibrium between solid solvent and vapor, at constant pressure,

$$\frac{d\ell nP_s}{dT} = \frac{L_s}{RT^2}$$

For an equilibrium between liquid and vapor, the corresponding equation is

$$\frac{d\ell nP_L}{dT} = \frac{L_e}{RT^2}$$

If it is assumed that the equations hold for supercooled solution in contact with solid, then

$$\frac{d\ell n(P_s/P_L)}{dT} = \frac{L_s - L_e}{RT^2} = \frac{L_f}{RT^2}$$

At the freezing point of the solution, the vapor pressure of the solid solvent must equal that of the solution, hence

$$\frac{d\ell n(P_1/P_L)}{dT} = \frac{L_f}{RT^2}$$

Since $P_1/P_L = X_1$ (mole fraction of solvent in solution) if Raoult's Law is applicable, then

$$\frac{d\ell nX_1}{dT} = \frac{L_f}{RT^2}$$

If this is integrated between T and T_o (where $X_1 = 1$)

$$\ell nX_1 = \frac{L_f}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

where T is the freezing point of the solution at solvent concentration X_1. This assumes that L_f is independent of temperature, which is not strictly true, but this approximation was used, since the normal variation of L_f with temperature would increase the freezing point depression in contrast to the real nonideality of the solutions, which tends to decrease the depression.

Using the last equation, the freezing point, T, was calculated for various concentrations of F_2 in OF_2 and OF_2 in F_2. A value of 122 cal/mole was used for the heat of fusion of F_2 (Reference 5). No value for the heat of fusion of OF_2 could be found in the literature, so it was estimated that the entropy of fusion was 6.5, which implies a heat fusion of 320 cal/mole. This value was used for the calculations

involved for constructing the phase diagram. A minimum freezing temperature of 39°K at an F_2 mole fraction of 0.65 resulted.

Solid fluorine is reported to undergo a transition at 45.55°K with a heat of transition of 173.9 cal/mole (Reference 5). Inasmuch as the solid fluorine can exist in two forms above the predicted eutectic temperature, the equilibrium diagram becomes more complicated. The theoretical phase diagram was recalculated using a value of 122 cal/mole as the heat of fusion of fluorine until the transition temperature was reached, after which the liquidus curve was assumed to undergo a change in slope corresponding to the heat of fusion plus the heat of transition. This curve was continued to meet the OF_2-rich liquidus curve leading to a theoretical minimum freezing point of 40°K at 0.54 mole fraction F_2.

APPARATUS

A Pyrex apparatus was designed and built for this experiment. It is illustrated in Figures 1 and 2. It consists of a central volume for the test chamber, fitted with inlet tubing, a solenoid operated stirrer, and a thermowell. The central tube is surrounded by several annuli arranged concentrically in the following order -- an annulus in which the pressure can be controlled to control heat transfer rates, an annulus for liquid helium to cool the fluids in test, an evacuated annulus, an annulus for liquid nitrogen (heat shield) and another evacuated annulus. The evacuated annuli were silvered except for strips for observation of the interior.

Liquid helium is supplied to the cooling bath from 25 liter transport Dewars connected to the apparatus by insulated lines. Liquid nitrogen was poured into the heat shield when needed.

Temperatures were measured with a copper-constantan thermocouple inserted in the thermowell with an external reference junction at liquid nitrogen temperature. Thermoelectric potentials were measured with a Grey type E-3067 potentiometer and temperatures estimated from the tables and data of Powell, Bunch, and Corruccini (Reference 6). The thermocouple calibration was checked against boiling liquid nitrogen and hydrogen as fixed points. At 50°K the thermoelectric emf for copper-constantan is about 12.1 microvolts per degree. With a sensitivity of 5 microvolts or better for the potentiometer, the sensitivity of temperature reading is about 0.4°.

MATERIALS

The oxidizers tested were obtained in the gaseous state from commercial suppliers. Fluorine supplied by Air Products and Chemicals was passed over an NaF absorption scrubber to reduce the HF content to 0.02 vol %. Oxygen difluoride supplied by Allied Chemical Division of General Chemical was also treated with NaF to remove HF.

PROCEDURE

The quantities of fluorine and oxygen difluoride were measured by volume in the liquid state; weights were calculated from reported (References 7 and 8) densities. A glass ampul of calibrated volume was attached to the oxidizer supply manifold. The system was evacuated, the measuring apparatus and the ampul were chilled with LN_2 to 77°K, the test apparatus was valved off, and the oxidizer supply was valved open. When sufficient oxidizer had condensed in the ampul, the supply was shut off, the line to the test unit was valved open, and the LN_2 was removed from around the ampul, causing the oxidizer to distill into the test apparatus. When distillation was complete, the ampul was valved off.

After condensation of oxidizer was complete, the solenoid stirrer was activated, liquid helium was supplied to the cooling bath, and the pressure in the heat-transfer annulus adjusted to attain a cooling rate of about 1°K/minute. The emf of the thermocouple was continuously monitored, and the value recorded at 30 second intervals. The appearance of the oxidizer was observed visually during the experiment.

The experiments were conducted with F_2, with OF_2, and with several mixtures of F_2 and OF_2. The recorded thermocouple potentials were converted to temperatures from which cooling curve graphs (temperature vs. time) were plotted for each solution concentration. Figure 3 is a typical example. Temperatures at which breaks in the curves occurred were identified, and these were plotted on a temperature vs. concentration graph to provide a typical phase diagram (Figure 4). The data used for plotting the phase diagram are tabulated in Table I.

RESULTS AND DISCUSSION

It was determined that, within the accuracy of the experiments, the binary system F_2-OF_2 exhibited typical eutectic formation with a probable break in the fluorine-rich liquidus curve due to a solid phase transition at 45 ± 0.5°K. The accuracy of the temperature measurements was ± 0.5°K. When the temperature-composition curves were plotted and extrapolated to their intersection (the eutectic), the error in composition was ± 2 mole %. This variation is indicated on the graphs by the bars through the experimental points. The errors in quantities of components used are believed to be considerably less than these. The eutectic temperature is estimated to be 43 ± 0.5°K and the eutectic composition 0.59 ± 0.02 mole fraction fluorine.

TABLE I

OBSERVED FREEZING POINTS -- OF_2-F_2 MIXTURES

	Mole % F_2	Initial F. P. °K	Transition Temp. °K	Eutectic F. P. °K
1.	100.0	53.0	-	-
2.	80.0	48.3	45.0	43.5
3.	69.5	-	45.0	42.4
4.	46.0	45.6	-	43.3
5.	28.0	47.8	-	43.4
6.	0	49.2	-	-

ACKNOWLEDGMENT

Work presented in this paper was conducted by the Douglas Aircraft Company, Missile and Space Systems Division, under company-sponsored research and development funds.

GLOSSARY

P = vapor pressure
L = latent heat
R = gas constant
T = temperature, °K

SUBSCRIPTS

s = solid state or solid-gas transition
L = liquid state or liquid-gas transition
e = evaporation
f = fusion
l = solution
o = freezing point of pure solvent

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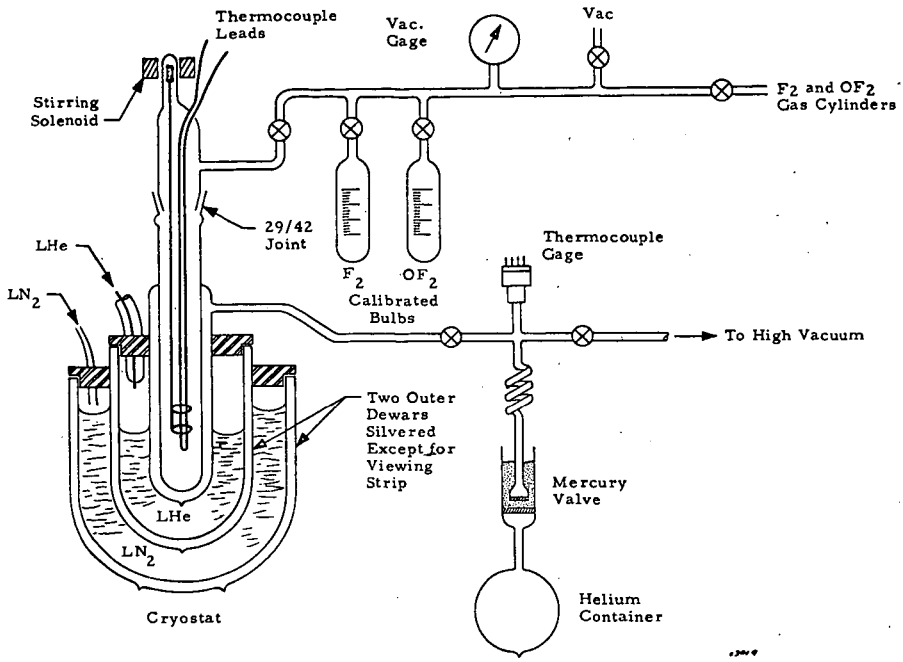

Figure 1. Freezing Point Apparatus

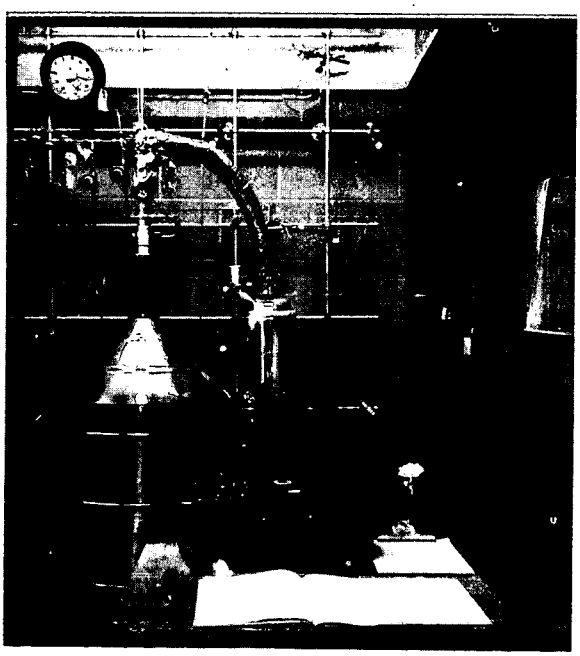

Figure 2. Freezing Point Apparatus

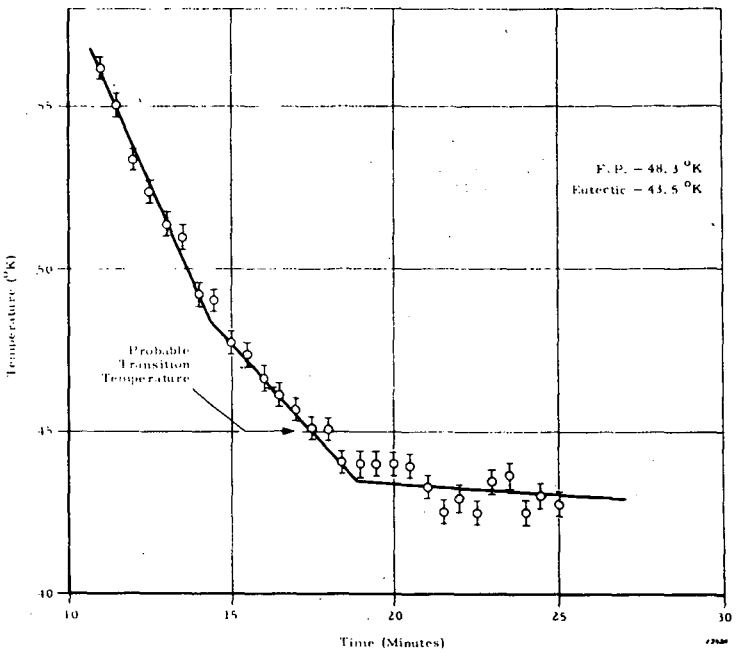

Figure 3. Cooling Curve — 80 mole % F_2, 20 mole % OF_2

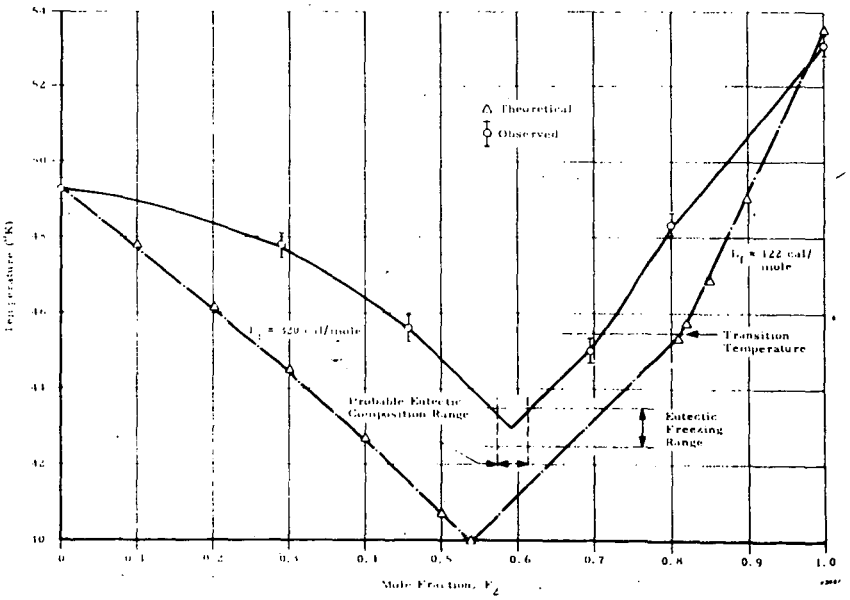

Figure 4. Phase Diagram, OF_2-F_2

REACTIONS OF OXYGEN TETRAFLUOROBORATE

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Introduction

Recently we developed an efficient method of preparing F_2O_2. This compound is known to react with boron trifluoride[1] to produce $O_2^+BF_4^-$. Little is known of the reaction of $O_2^+BF_4^-$ itself. It is relatively stable at room temperature, but reacts readily with organic compounds. For instance, tiny particles dropped into benzene or isopropyl alcohol instantly ignite fires. The only known inorganic reaction[1] is with NO_2 where oxygen is displaced giving $NO_2^+BF_4^-$. This paper describes some additional reactions of $O_2^+BF_4^-$ with inorganic as well as some organic compounds.

Results and Discussion

A. Inorganic Reactants

1. Xenon

Since xenon has nearly the same ionization potential as O_2, and since Xe^+ should be smaller than O_2^+, we felt that possibly xenon would replace oxygen to give the novel $Xe^+BF_4^-$. When liquid xenon (165°K) and solid $O_2^+BF_4^-$ ($Xe/O_2^+BF_4^- = 15$) were mixed in an evacuated tube, oxygen was released. The reaction was accomplished by allowing the xenon alternately to vaporize and condense around the $O_2^+BF_4^-$. After several minutes the sample was cooled in liquid nitrogen and any non-condensable gases were expanded into a fixed volume. The mass spectrum of the expanded gases showed only oxygen. The oxygen was pumped off; the reaction tube was warmed enough to liquefy the xenon and the procedure was repeated. This was continued until no further oxygen was obtained (about 85% of theory). Then the xenon was vaporized at 173°K (any BF_3 would also vaporize at this temperature) and expanded into a fixed volume. The loss of xenon (the amount reacted) was the same as the amount of oxygen collected. The mass spectrum indicated essentially no BF_3 was in the expanded xenon.

After removing all the xenon, the remaining white solid was slowly warmed. Decomposition became appreciable at 253°K with complete decomposition at room temperature. The mass spectrum of the gases showed Xe, BF_3, and F_2 with a $Xe:BF_3$ ratio of 1; we believe this to be evidence for the existence of $Xe^+BF_4^-$. Some O_2 was observed as well. The oxygen could have come from the decomposition of some unreacted $O_2^+BF_4^-$, or possibly from a xenon-oxygen compound of low stability. It is a firm conclusion that xenon reacts with $O_2^+BF_4^-$ at temperatures as low as 165°K to give free oxygen and a xenon compound.

2. Chlorine Dioxide

Chlorine dioxide was prepared by dropping sulfuric acid onto a mixture of $KClO_3$ and glass chips. The ClO_2 generated was then diluted in a stream of CO_2 and passed first through a drying tube (P_2O_5), then through a sample of

$O_2^+BF_4^-$ which was supported on a glass frit and cooled to 195°K. An immediate reaction occurred, releasing oxygen. Within minutes the reaction was completed. The product, a light-yellow solid, was unstable at room temperature. The mass spectrum of its decomposition products showed only m/q peaks for fragment ions from ClO_2, BF_3 and F_2. The product $ClO_2^+BF_4^-$ has previously been reported[2] from the reaction of chloryl fluoride with boron trifluoride.

3. Chlorine, Chlorine Trifluoride, and Ammonia

In hopes of preparing the novel $Cl_2^+BF_4^-$, $ClF_3^+BF_4^-$, and $NH_3^+BF_4^-$, we passed the corresponding gases through $O_2^+BF_4^-$. In each case oxygen was displaced. However, the products were not stable at the reaction temperature (223°K to 195°K).

4. Cyanogen

At 248°K, $O_2^+BF_4^-$ dissolved in liquid cyanogen to give a clear, colorless solution. However, no oxygen was displaced and $O_2^+BF_4^-$ was recovered after removal of the cyanogen.

B. Organic Reactants

Although benzene and isopropyl alcohol spontaneously inflame when a milligram of $O_2^+BF_4^-$ is added, we felt that reactions with other specific organic compounds (in particular perhalogenated materials) could be studied under carefully controlled conditions.

Indeed, when liquid CCl_4 was condensed around $O_2^+BF_4^-$ at 250°K, a smooth reaction occured to liberate O_2, Cl_2, and BF_3, forming $CFCl_3$ and CF_2Cl_2. In a like manner, $O_2^+BF_4^-$ reacted with CF_2Cl_2 at 233°K to form CF_3Cl, essentially quantitatively. No CF_4 was detected. Hexafluorobenzene also reacted with $O_2^+BF_4^-$ at 298°K to give O_2, F_2, BF_3, and fluorinated hydrocarbons with the following prominent ions in the mass spectrum: CF_3^+, $C_2F_4^+$, $C_2F_5^+$, and $C_3F_5^+$. Some oxygen was converted to CO_2 and COF_2. It was also found that methane and ethane will inflame at 195°K. However, there was no reaction between perfluorocyclobutane and $O_2^+BF_4^-$.

Of the compounds that were found to react readily with $O_2^+BF_4^-$, both methane and ClF_3 have higher ionization potentials than that of O_2 (12.2 ev). Cyanogen, with both unsaturation and a higher ionization potential, did not react. In the case of compounds with ionization potentials below or equal to that of O_2, a reasonable mechanism for reaction is electron transfer to liberate O_2 and form a new ion which may or may not react further.

It should be noted that no CF_4 was formed from the reaction of $O_2^+BF_4^-$ with CCl_2F_2, whereas CCl_2F_2 was a product from the reaction with CCl_4. This would be expected if the primary products from the unstable $CCl_2F_2^+BF_4^-$ and $CCl_4^+BF_4^-$ were $CClF_3$ and CCl_3F, respectively. The former product has a higher ionization potential (12.9 ev)[3][4] than O_2 and is less likely to react with $O_2^+BF_4^-$. Therefore no CF_4 was observed. On the other hand, CCl_3F has a favorable ionization potential, and further reaction with $O_2^+BF_4^-$ is possible, giving CCl_2F_2.

Acknowledgement

This work was supported by the Advanced Research Projects Agency under the research contract No. DA31-124-ARO(D)-54, monitored by the U.S. Army Research Office, Durham, North Carolina.

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PREPARATION OF FLUORINE PEROXIDES AND DIOXYGEN TETRAFLUOROBORATE BY LOW TEMPERATURE RADIOLYSIS

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Introduction

More than three decades have elapsed since it was shown that oxygen and fluorine could be combined by passage through an electrical discharge. The product, condensed on a very cold surface, was dioxygen difluoride, O_2F_2.[1] More recently, higher oxides of fluorine have been similarly prepared; these have been claimed to be O_3F_2,[2] O_4F_2,[3] O_5F_2 and O_6F_2.[4] The existence of O_4F_2 appears to be well established; however, there has been some controversy concerning the existence of O_3F_2 as a molecular species.[5]

Although O_2F_2 and O_4F_2 are stable only at very low temperatures, considerable evidence has been acquired concerning their physical[6-10] and chemical[11-16] properties. With all these studies the method of preparation of the oxygen fluorides has remained the same. No work has been reported on the radiation-induced reaction of oxygen and fluorine in a condensed phase.

The present study describes the reaction of these materials in the liquid phase at 77°K. Reactions were induced by high intensity 3 Mev bremsstrahlung.

Procedure

Except for certain cases, ca 1.0 ml samples (28 mmoles) were irradiated in vacuo in stainless steel or sapphire vessels at 77°K for 1-2 hr at dose rates up to 100 megarads/hr of 3 Mev bremsstrahlung. The high-intensity 3 Mev bremsstrahlung was generated by directing the 3 Mev, 1 ma unscanned electron beam from a Van de Graaff accelerator onto a water-cooled gold target.[17] Following the irradiation the reaction vessel was attached to a vacuum line with provisions for expanding into a predetermined volume, measuring the pressure and analyzing with a mass spectrometer.[18] With this equipment the total volume and composition of gases from decompositions of products could be measured.

In experiments where BF_3 was added to the irradiated sample, the BF_3 was condensed in the top of the irradiated sample tube. The dewar of liquid nitrogen surrounding the tube was then slowly lowered to distill the BF_3 to the bottom of the tube. By this method any material deposited on the walls of the reaction vessel could react with the BF_3. The excess oxygen and fluorine were removed at 77°K; the sample tube was warmed to 195°K and the unreacted BF_3 was pumped off.

Results and Discussion

The initial mixtures of F_2 and O_2 had a yellow color; after irradiation a reddish-brown solid was observed on the walls of the sapphire tube. The solid is presumed to be a mixture of F_2O_2 and F_2O_4 with possibly other oxides of fluorine. In each of the experiments described below (Table 1), excess F_2 and O_2 were removed at 77°K, first by evaporation into the calibrated

volume and then by pumping to a few microns pressure; this treatment would also remove F_2O. The sample was then warmed cautiously to decompose the F_2O_4 to F_2O_2; the O_2 released was measured gasometrically. This operation was carried out most successfully by removing the liquid nitrogen bath until a small increase in pressure was observed, replacing the liquid nitrogen, and repeating the process until the F_2O_2 could be melted (113°K) without further oxygen evolution. The oxygen thus evolved was mass spectrometrically free of F_2 (however, this was not a very sensitive test because the mass spectrometer inlet system was somewhat reactive with small quantities of fluorine). The blood-red liquid F_2O_2 was then frozen at 77°K (orange solid) and the residual O_2 was pumped away. Subsequent remelting at 113°K resulted in no further release of O_2. The sample was then warmed slowly to room temperature to decompose the F_2O_2 and measure the $F_2 + O_2$.

This procedure was occasionally unsuccessful in cases with the initial mole ratio F_2/O_2 of 1.0 or 3.0, because a minor explosion ("pop") would be heard during the decomposition of F_2O_4, accompanied by a sudden rise in pressure. The gasometric data indicated that in these cases some of the F_2O_2 was decomposed during the sudden decomposition of F_2O_4. Because of this, the apparent yields of F_2O_4 and F_2O_2 reported in Table 1 are taken only from experiments in which there was no audible evidence of explosion. Nevertheless, the reported yields of F_2O_4 may be slightly too high in some cases because of some decomposition of F_2O_2 during the decomposition of F_2O_4.

The data reported in Table 1 show several unusual features. First, in the mixtures containing only F_2 and O_2, the number of millimoles of oxygen converted to F_2O_2 and F_2O_4 remain nearly constant despite a large variation in the initial ratio of F_2 to O_2, even when the major part of the oxygen was consumed. The G-value for products also remained constant at a value that is several-fold higher than the values that are usually found for non-chain reactions.[8] These observations suggest that the formation of F_2O_2 under these conditions involves a short chain process that is initiated with approximately equal efficiency whether the initial absorption of energy is done by oxygen or by fluorine.

Another observation is that the ratio of F_2O_4 to F_2O_2 in the products displays no obvious trend with the initial ratio of F_2/O_2. The possible chain

$$\begin{array}{ccccccc} F\cdot & \xrightarrow{O_2} & FO_2\cdot & \xrightarrow{O_2} & FO_4\cdot & \xrightarrow{O_2} & FO_6\cdot \\ \downarrow F\cdot & & \downarrow F_2 & & \downarrow F_2 & & \downarrow F_2 \\ F_2 & & F_2O_2 + F\cdot & & F_2O_4 + F\cdot & & F_2O_6 + F\cdot \end{array}$$

would not lead to these results in a homogeneous system, but the kinetics are probably complicated by the fact that the products precipitate as solids.

The experiments in which the reactants were diluted with argon show that the presence of argon had a small positive effect on the total conversion of oxygen, whereas dilution with nitrogen does not appear to effect the yield. Some energy transfer from argon seems indicated.

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a) G for ion pair formation is expected to be about 4; for radicals it often ranges from 6-10.

One experiment was done with a large excess of oxygen (F_2/O_2 = 1/6). The unreacted F_2 and O_2 (21.6 mmoles out of an initial 28) were removed and the reaction tube evacuated to < 5 μ. The color of the solid remaining in the sapphire tube was very dark brown. When the liquid nitrogen bath was momentarily removed and the sample was illuminated briefly with a flashlight, the product detonated violently and shattered the sapphire tube. Whether the detonation was due to the presence of a large amount of F_2O_4 or to F_2O_6 is not known. It is unlikely that the detonation was due to O_3 since its vapor pressure is well above 5 μ at 77°K and should have been pumped off. The very unstable F_2O_6 (dark brown in color) has been reported to explode on illumination or sudden warming. It is claimed to decompose thermally about 90°K.

In the experiments listed in Table 1, some F_2O was formed in addition to F_2O_2 and F_2O_4; the amount was relatively small and was not studied systematically. The presence of F_2O was detected by mass spectrometric analysis.

Experiments With Added BF_3

It has been shown by others[15] that BF_3 reacts with F_2O_2 at low temperatures to form the ionic compound $O_2^+BF_4^-$. We therefore added BF_3 to irradiated mixtures of O_2 and F_2 in order to explore the radiation route to $O_2^+BF_4^-$ and possibly to $O_4^+BF_4^-$.

Boron trifluoride (3.5 mmoles) was condensed in the top of the irradiation tube containing the formed fluorine peroxides (ca 1.7-2.0 millimoles) suspended in the excess fluorine and oxygen. The BF_3 was distilled to the bottom of the tube and the contents mixed by alternately vaporizing and condensing a portion of the excess fluorine and oxygen. In this manner the BF_3 was better able to contact the reddish-brown peroxide. The excess fluorine and oxygen were then removed under vacuum at 77°K. When the contents were warmed to 113°K, a rapid reaction occurred, and the color changed to orange. This suggests that much of the F_2O_4 decomposed without reacting with BF_3. The orange color changed to white when the temperature was raised to 143°K; this corresponds to the conversion of the F_2O_2 to $O_2^+BF_4^-$. Further warming to 240°K led to slight decomposition; the remaining solid was relatively stable, decomposing only very slowly at room temperature and atmospheric pressure. The decomposition is much more rapid under reduced pressure, indicating a reversible step with a gaseous product in the decomposition. The yield was measured by recovering the solid in a dry box and weighing it.

The gases evolved upon warming to 240°K consisted of O_2, F_2, and BF_3. Irradiation of various fluorine-oxygen mixtures followed by addition of BF_3 gave gases for this low-temperature decomposition in the ratio of $(O_2 + F_2)/BF_3$ of 1.9 ± .35. There is a systematic tendency for this ratio to be higher when the total volume of gas liberated is low. These findings correspond to decomposition of an oxygen-rich compound, probably $O_4^+BF_4^-$, with simultaneous induced decomposition of some of the $O_2^+BF_4^-$. (Evidence for the formation of $O_4^+BF_4^-$ from F_2O_4 has also been obtained in an independent investigation by Soloman and his colleagues.)[19]

The more stable product (presumed to be $O_2^+BF_4^-$) decomposed rapidly above 300°K to give O_2, F_2, and BF_3. The elemental analysis of the solid was F, 62.6%; B, 8.6%; theory, F, 63.7%; B, 9.2%). The infrared spectrum of the powder between silver chloride plates exhibits the characteristic absorption frequencies[20] of the BF_4^- ion. No absorption band attributable to O_2^+ was observed, but this ion should have no dipole moment.

The x-ray powder pattern (Table 2) is very similar to that of the likely isomorphous $NO^+BF_4^-$ compound. (The nitrosyl and dioxygenyl cations are similar in size.)[21] A comparable correlation[14] was found for $NO^+AsF_6^-$ and $O_2^+AsF_6^-$.

The EPR spectrum of the solid at 77°K was a broad signal with a G-value of 1.94 and a peak-to-peak separation in the derivative mode of about 382 gauss. Kirshenbaum and Grosse[22] found similar results in HF solution. Soloman, et al[15][23] reported similar results for the solid.

The yields of $O_2^+BF_4^-$ recovered from various experiments are listed in Table 3. Comparison of the yields after 1 hr irradiation time in the experiments listed in Tables 1 and 3 indicates that a little less than two moles of F_2O_2 are required to produce one mole of $O_2^+BF_4^-$. Either some decomposition of F_2O_2 occurred during the process of warming to the temperature of reaction with BF_3, or the formation of $O_2^+BF_4^-$ is accompanied by a side reaction that decomposes part of the F_2O_2. It will also be noted that in the single experiment with a large excess of oxygen present during irradiation ($F_2/O_2 = 1/6$), the excess F_2 and O_2 were successfully removed without detonation after BF_3 was added. The yield of $O_2^+BF_4^-$ was relatively small, but there was evidence for the formation of larger amounts of a less stable compound. One other observation of interest is that when BF_3 is present during the irradiation, the yield of $O_2^+BF_4^-$ finally recovered is relatively small.

Acknowledgements

This work was supported by the Advanced Research Projects Agency under the research contract No. DA31-124-ARO(D)-54, monitored by the U.S. Army Research Office, Durham, North Carolina. Gratitude is also expressed to Dr. R. M. Curtis for performing the x-ray studies on $O_2^+BF_4^-$, to Dr. E. E. Genser for obtaining the EPR spectrum of $O_2^+BF_4^-$, and to Mr. E. Wong for his assistance with the Van de Graaff accelerator.

Table 1. YIELDS OF F_2O_2 AND F_2O_4 FROM IRRADIATION[a] OF FLUORINE/OXYGEN MIXTURES

Mole Ratio, F_2/O_2	Amount Irradiated, millimoles				Yield,[b] millimoles		Ratio, F_2O_4/F_2O_2	Oxygen Consumed		G-Value (c)
	F_2	O_2	Ar	N_2	F_2O_2	F_2O_4		mmole	%	
1	14.0	14.0	-	-	1.50	0.13	0.087 ± 0.02	1.72	12.3	17.5
3	21.0	7.0	-	-	1.72	0.085	0.05 ± 0.02	1.89	27.0	18.5
5	22.8	4.6	-	-	1.93	0.105	0.055 ± 0.02	2.14	46.6	21.2
7	24.5	3.5	-	-	1.86	0.14	0.075 ± 0.015	2.14	61.2	20.6
1	10.5	10.5	-	7.0		(d)	n.d.	1.26	12.0	13.5
1	10.5	10.5	7.0	-		(d)	n.d.	1.73	16.5	17.1
1	10.5	10.5	7.0	-	1.65	0.07	0.042 ± 0.02	1.79	17.1	17.6
3	15.7	5.3	7.0	-	1.62	0.14	0.09 ± 0.02	1.90	35.9	18.2
5	17.5	3.5	7.0	-	1.62	0.105	0.065 ± 0.02	1.83	52.3	17.3
7	18.4	2.6	7.0	-	1.62	0.09	0.055 ± 0.02	1.79	68.9	16.8

a) 77°K, 100 megarads, 1 hr.
b) Yield data accurate to ca ± 0.03 mmole.
c) Molecules of product formed per 100 ev absorbed energy.
d) Amount of F_2O_4 not reliably determined because of a slight detonation on warming the system to decompose F_2O_4.

Table 2. DIFFRACTION PATTERNS OF $NO^+BF_4^-$ AND $O_2^+BF_4^-$

$NO^+BF_4^-$		$O_2^+BF_4^-$		
Interplanar Spacing A	Intensity of Reflection	Interplanar Spacing A	Intensity of Reflection	hkl
5.50	24	5.50	16	110
4.41	40	4.33	34	101
3.96	8	3.91	5	111
3.76	12	3.74	9	120
3.51	100	3.47	100	021
3.25	12	3.27	16	210
3.13	80	3.10	88	121
2.82	60	2.82	75	211
2.75	12	2.74	12	220
2.52	40	2.49	44	112
2.40	3	2.43	7	131
2.39	8	2.35	7	022
2.26	60	2.24	63	122

Table 3. PREPARATION OF $O_2^+BF_4^-$ [a]

Irradiation Time, min[b]	Ratio $F_2:O_2$ Irradiated[c]	$O_2^+BF_4^-$ Produced, mg	%m $O_2^+BF_4^-$ Based on Oxygen	G-Value Total[g]
15	1:1	27	1.6	8.9
30	1:1	53	3	8.8
60	1:1	96	6	7.9
60	2:1	129	12	11.0
60	3:1	134	16	10.6
60	5:1	127	24	10.5
60	7:1	113	27	8.8
60	1:6	44[d]	1.5	4.1
60[e]	1:1	45	2.7	14.9
120	3:1	216	26	8.6
180	1:1	231	14	6.3
180	5:1	248	47	6.9
120[f]	3:1	21	2.6	0.2

a) 14 mmoles of BF_3 was added after irradiation.
b) Dose rate of 100 megarads/hour.
c) Millimoles of oxygen used with $F_2:O_2$ ratios was: 1:1 = 14 mmoles; 2:1 = 8.75 mmoles; 3:1 = 7.0 mmoles; 5:1 = 4.4 mmoles; 7:1 = 3.5 mmoles; 1:6 = 21.9 mmoles.
d) A second compound was formed which decomposed at 133°K yielding about 3 mmoles of noncondensable gases.
e) Dose rate of 25 megarads/hour.
f) 10.5 mmoles of BF_3 added to the reaction tube before irradiation.
g) Molecules of product formed per 100 ev absorbed energy.

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REVIEW OF ADVANCED INORGANIC OXIDIZERS

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I. Introduction

In this paper the properties and chemistry of advanced inorganic oxidizers will be reviewed with emphasis on recent developments. The classes of compounds will be limited to the oxygen fluorides, the nitrogen fluorides, the nitrogen fluoride oxides, the halogen fluorides and the halogen fluoride oxides. In general, all of the compounds described here are highly reactive, toxic materials, and very volatile except for ionic derivatives. The growth of chemistry involving O-F, N-F and Cl-F compounds has been remarkable: from about nil in 1946 to over 1000 today.

II. Oxygen Fluorides and Derivatives

The reported oxygen fluorides, their derivatives and some of their properties are summarized in Table I. Oxygen difluoride is the only binary compound of this type which is stable at room temperature, but O_2F_2 is stable below about -80°C and is well characterized. A reasonably good understanding has been gained recently of the apparent equilibrium system $O_4F_2 \rightleftharpoons 2O_2F$.

The existence of O_3F_2 as a separate entity is in doubt, and the natures of the reported "O_5F_2" and "O_6F_2" are quite uncertain. Oxygen difluoride is commercially available, while the others are prepared by electrical discharge at low temperatures from appropriate O_2-F_2 mixtures.

The structures of OF_2 and O_2F_2 have been determined and are compared in Figure 1 with those of related compounds. The abnormally long O-F distance and the greatly shortened O-O bond in O_2F_2 have led Linett to formulate its structure as having an essentially four-electron O-O bond (as in O_2 itself, 1.21 Å bond length) and a one-electron O-F bond (resonating between the two positions). Dioxygen difluoride can, therefore, readily dissociate at the O-F bond to give F atoms and the stable O_2F radical:

$$O_2F_2 \longrightarrow O_2F\cdot + F\cdot$$

and is an extremely energetic fluorinating agent. At low temperatures it is more reactive than fluorine itself and far more reactive than OF_2. The latter compound begins to decompose near 200°C and many of its reactions require activation by heat or light. The $O_2F\cdot$ radical can be generated by ultraviolet radiation of liquid OF_2, of OF_2-O_2, F_2-O_2 or F_2-N_2O mixtures in a matrix, at 4°K, by the decomposition of O_4F_2 or FSO_2OOF, and in the reaction of CF_4 with O_2. The OF radical has never been detected in the gas or liquid phase despite an intensive search.

The reactions of the oxygen fluorides are usually simple fluorinations, but oxygen addition by OF_2 can occur especially in aqueous solution or in reactions

TABLE I

OXYGEN FLUORIDES AND DERIVATIVES

Compound	Properties				
	MP, °C	BP, °C	Decomp. Temp.	^{19}F NMR[a]	Infrared[b]
OF·	Observed in N_2 or Ar matrix at 4°R			--	1028
OF_2	-223.8	-144.8	~200	-249 liq. -248 g	1740, 929, 909, 880, 826, 461
O_2F_2	-163.5	-57 dec.	-78	-865 -825	1024, 628, 463
$O_4F_2 \rightleftharpoons 2O_2F\cdot$	-191	-80 ext	-183	--	1519, 588 (O_4F_2) 1494, 484 ($O_2F\cdot$)
"O_3F_2"	-189 to 190	-60 dec.	<-158	-857	--
"O_5F_2"	<-196	--	--	--	--
"O_6F_2"	<-213	--	--	--	--
CF_3OF	<-215	-95	--	72, -147	1282, 1259, 1223, 1217, 945, 880, 679
$CF_2(OF)_2$	--	-62.5	--	-159 tr, +84.2 tr	1300, 1270, 1150, 950 qt
$CF_3C(O)OF$	--	-21 -21.5	--	--	--
SF_5OF	-86	-35	--	-189	935, 888, 614, 585
NO_2OF	-175	-45.9	--	--	1760, 1300, 920, 810, 708
ClO_3OF	-167.3	-15.9	--	-226	1298, 1049, 666
FSO_2OF	-158.5	-31.3	--	-244.9, -36.2	--
CF_3OOF	--	-50 (est)	--	+69.2 db, -291.5 qt	1290, 1175, 955, 755, 725
C_2F_5OOF	--	-15 (est)	--	+84.1 db of tr (CF_3) +97.4 db of qt (CF_2) -291.6 tr of qt	1380, 1285, 1235, 1175, 740
FSO_2OOF	--	0	--	--	--

a/ ^{19}F chemical shift (ppm vs. $CFCl_3$=0) for fluorine of -OF group.
b/ Positions (cm^{-1}) for O-F stretching fundamental.

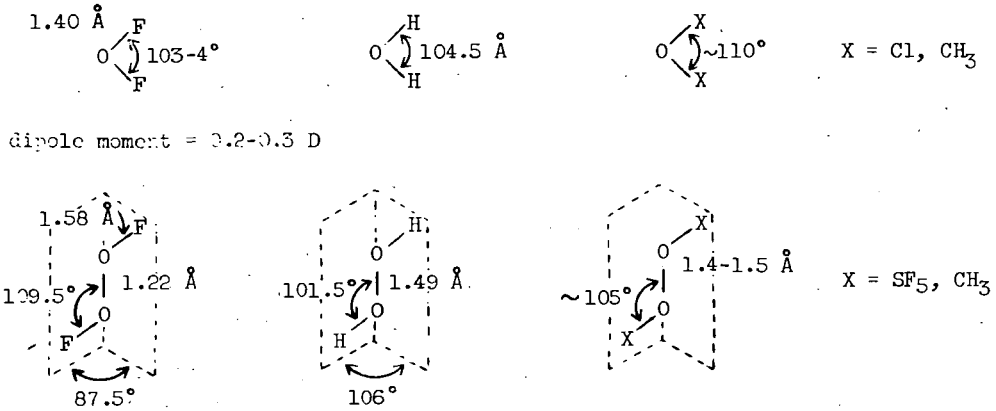


Figure 1 - Comparison of Structures of OF_2, O_2F_2 and Related Compounds

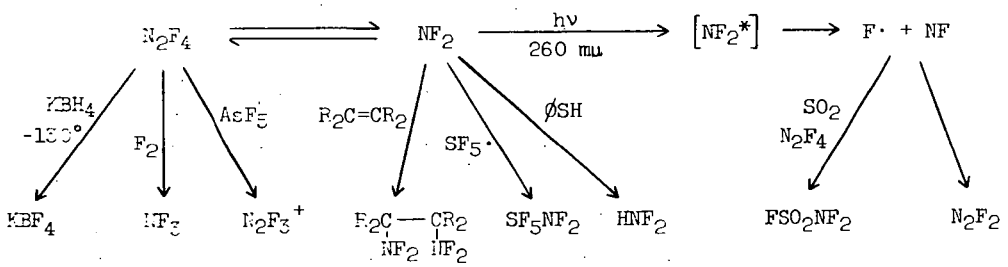


Figure 2 - Examples of Reaction Types for N_2F_4

with some nitrogen, chlorine, or sulfur-containing materials. Dioxygen difluoride (or the O_2F radical) undergoes the fluoride abstraction reaction with strong Lewis acids at low temperatures to give stable dioxygenyl salts. Oxygen difluoride undergoes a similar reaction at elevated temperatures.

$$O_2F_2 + BF_3 \xrightarrow{-140^\circ} O_2BF_4 + 1/2F_2$$

$$2OF_2 + SbF_5 \xrightarrow{200^\circ} O_2SbF_6 + F_2$$

Although considerable doubt now exists about the existence of trioxygen trifluoride, the trifluoromethyl derivative CF_3OOOCF_3 is known as well as the peroxide CF_3OOCF_3. The authors are not aware of reports of the simple ether $(CF_3)_2O$, although the sulfide $(CF_3)_2S$ is stable at 400°C.

III. Nitrogen Fluorides and Derivatives

The reported nitrogen fluorides, their derivatives and some of their properties are summarized in Table II.

The NF molecule is known only as a reactive intermediate which dimerizes readily to N_2F_2. It has been observed by flash photolysis of the NF_2 radical in an argon matrix at 4°K and by pyrolysis of N_2F_4 at high dilution in argon at 2550°K.

The NF_2 radical is well established to exist in equilibrium with N_2F_4 in analogy to the N_2O_4-NO_2 equilibrium

$$N_2F_4 \rightleftharpoons 2NF_2$$

The structure of NF_2 (N-F = 1.36 Å; ∠FNF = 103°) is closely related to that of NF_3. The NF_2 radical has fundamental stretching frequencies at 1074 and 935 cm^{-1} in the infrared. In the ultraviolet, NF_2 absorbs at 260 mμ to give an excited radical, NF_2*, which decomposes to NF and F·, but may undergo unique reactions. The reactions of NF_2 are discussed in the section on N_2F_4.

Nitrogen trifluoride is commercially available and its properties are well known. It has an ammonia-like structure with N-F = 1.37 Å and ∠FNF = 103°. Only 57 kcal/mol are required to dissociate a F· atom from NF_3, but an average of 71 kcal/mol are required for each of the remaining two N-F bonds of the stable NF_2 radical. NF_3 is relatively unreactive at mild temperatures, but functions as a fluorinating agent at elevated temperature. The most interesting reaction of NF_3 to be reported recently is that with fluorine and Lewis acids to give stable salts of the NF_4^+ ion.

$$NF_3 + F_2 + AsF_5 \xrightarrow[-80^\circ]{\text{elect. disc.}} NF_4^+AsF_6^-$$

$$NF_3 + F_2 + SbF_6 \xrightarrow[3000\ psi]{300^\circ} NF_4^+SbF_6^-$$

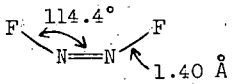
Difluorodiazine is now well established to exist in the cis and trans isomeric forms and the properties and structures of each are known.

TABLE II

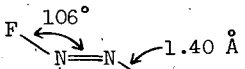
NITROGEN FLUORIDES AND DERIVATIVES

Compound	MP, °C	BP, °C	^{19}F NMR	IR
NF_2	--	--	--	1070, 931
NF_3	-208.5	-129	-142	1031, 1010, 907, 642
N_2F_2 (cis)	-195	-105.7	-129	1524db, 952tr, 896db, 737tr
(trans)	-172	-111.4	-88	989 (1996m, 1581m, 1434m)
N_2F_4	-164.5	-73	-58	1010, 998, 959, 946
N_3F	-154	-82	--	--
NFO	-132.5	-59.9	-479	1844, 766, 521
NFO_2	-166	-72.5	-393	1793, 1312, 822, 742, 570
NF_3O	-160	-85	-363	1687, 887, 743, 528
NF_2NO	--	dec.	-65	--
HNF_2	-116 ± 3	<23.6	6	3193w, 1428db, 1280db, 978db
$ClNF_2$	-183	-67	-141	920tr, 853db, 694tr
Cl_2NF	-10 to 0 (est.)		--	--
N_2F^+			-103	1050
$N_2F_3^+$			-144 (db.)	1521, 1304, 1128, 924, 518,
			-192	497
NF_4^+			-214.7 (tr.)	1163, 611
NF_2O^+			-331	1857, 1162, 905

Other derivatives include compounds of the types: MNF_2 (M = SF_5-, SF_5O-, CF_3SF_4-, FSO_2-, FSO_2O-, CF_3S-); $R(NF_2)_X$ (R = R_f, alkyl, anthracene, etc.; X = 1-4); R-C(=NF)-R'; and R-N(O)=NF.



1.21 Å 0.17 D



1.22 Å

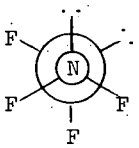
The N-F bond is lengthened over that in NF_3 and the N=N bond is shortened compared to that (1.24 Å) in $N_2(CH_3)_2$. The N-F and N=N bond energies of the trans form is 68 and 109 kcal/mol, respectively. The trans N_2F_2 is conveniently prepared by reaction of N_2F_4 at low pressure with $AlCl_3$ at -80°. The trans form is converted to the cis form in over 90% yield at 75° in a well-passivated stainless steel cylinder. The N_2F_2 is obtained nearly quantitatively by the decomposition at 20° of the complex $KF \cdot HNF_2$ formed at -80°C. Difluorodiazine has also been offered commercially. The cis N_2F_2 is more reactive chemically than trans N_2F_2, but both can act as fluorinating agents. The so-called N=N double bond is unusually inert and does not undergo addition reactions. Detonations, especially with the cis isomer, have occurred upon application of high pressure. The fluorination of N_2F_2 to N_2F_4 has apparently not been reported. cis-N_2F_2 undergoes the fluoride abstraction with Lewis acids to give a stable salt of the N_2F^+ ion

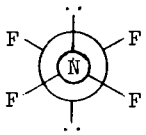
$$N_2F_2 + AsF_5 \longrightarrow N_2F^+AsF_6^-$$

The trans isomer also gives this reaction with SbF_5.

Tetrafluorohydrazine has the structure in the gas phase on the left below (d and l isomers) but the symmetrical isomer on the right has also been observed in the liquid at low temperature.

N-F	1.39 Å
N-N	1.53 Å
∠ FNF	104°
∠ NNF	102°
dihedral angle	69°
^{19}F NMR	-65.2, -53.2, -44.0, -31.9 ϕ
(in NF_3 at -155°)	





-60.4 ϕ

The abnormally long N-N bond (compared to 1.45 Å in N_2H_4) has a low dissociation energy (20 kcal/mol) and N_2F_4 exists in equilibrium with stable NF_2 radicals. Tetrafluorohydrazine has been available commercially since 1960 and its reactions have been studied intensively. It enters into at least five types of reactions: (1) normal NF_2 radical reactions including addition to olefins or a second radical, and abstraction reactions; (2) excited NF_2 reactions resulting from photolysis at about 260 mμ; (3) fluorination (oxidation) reactions; (4) reduction reactions; (5) fluoride abstraction reaction. Examples of each are illustrated in Figure 2.

Trifluoramine oxide, NF_3O, was reported in 1965. It can be prepared by electric discharge at -196° in mixtures of NF_3 and O_2 or OF_2, by the flame fluorination of NO with fast quench, or more conveniently at 25° by the fluorination of NO with F_2 photochemically or with certain metal hexafluorides such as IrF_6. The NF_3O has a tetrahedral structure in which the N-F and N → O bonds are slightly

weaker than those in NFO_2. The NF_3O has good thermal and hydrolytic stability, but undergoes the fluoride abstraction reaction with strong Lewis acids, to give salts such as $NF_2O^+AsF_6^-$, and adds to perfluoroolefins (under BF_3 catalysis) to give stable R_fONF_2 compounds. It apparently reacts slowly with NO to give NOF.

Difluoramine has an ammonia-like structure with the following parameters: N-H, 1.03-1.08; N-F, 1.38; FNF, 103°, HNF, 102°; dipole moment, 1.93 D. It is best prepared from difluorourea (which is obtained by aqueous fluorination of urea) by treatment with H_2SO_4 at 90° or by the reaction of N_2F_4 with C_6H_5SH at 50°. The HNF_2 is stable and can be stored, but the usual procedure is to generate it as needed and pass it directly into a reaction vessel, since it has a tendency to explode when frozen. The reactions of HNF_2 are usually complex, but it undergoes three general types of reactions as follows: oxidation, for example with aqueous Fe^{+3} solution to give N_2F_4 (perhaps the NF_2^- ion is involved); reduction, as in the reaction with aqueous HI to give NH_4F and HF; complex formation with ethers, Lewis acids, and metal fluorides.

Chlorodifluoramine $ClNF_2$ is well known, Cl_2NF and $BrNF_2$ are known as unstable compounds, and the other halogen fluoramines appear to be very unstable. The $ClNF_2$ (or $BrNF_2$) can be prepared by the reaction of aqueous NaOCl (or NaOBr) with N,N-difluorourea or N,N-difluorosulfuryl amide. The Cl_2NF is prepared by the reaction of ClF with ClN_3 at 25°C or with NaN_3 at 0°. The $ClNF_2$ is stable but dissociates readily to give Cl atoms and NF_2 radicals (which defines the reaction chemistry) while Cl_2NF is explosively unstable in the liquid state.

A few remaining N-F compounds such as NF_2NO and N_3F are of limited interest, but a number of inorganic compounds and a host of organic compounds have been prepared in recent years in which NF_2 groups may be regarded as substituents, e.g., SF_5NF_2, $C(NF_2)_4$, $C(NF)(NF_2)_2$, CF_3ONF_2 and $CF_3N(O)=NF$.

A summary of the interconversions of the nitrogen fluorides is found in Figure 3.

Chlorine Fluorides and Related Compounds

The halogen fluorides of prime interest as propellant oxidizers have been ClF_3, ClF_5, ClO_3F and BrF_5, but a number of other halogen fluorides have been studied. Properties of halogen fluorides are summarized in Table III.

Chlorine monofluoride appears to have considerable ionic character as reflected in the ^{19}F NMR chemical shift of ϕ = +441 ppm (vs. $CFCl_3$). The Cl-F bond distance is 1.63 Å, the dipole moment, 0.88 D, the bond dissociation energy, 60.4 kcal/mol, and the heat of formation, -13.5 kcal/mol. The ClF is an energetic fluorinating agent. It reacts with fluorides such as CsF or NOF to give $Cs^+ClF_2^-$ and $NO^+ClF_2^-$, respectively, and has been reported to react with the Lewis acid AsF_5 to give $Cl^+AsF_6^-$ but substantiating evidence is lacking. The high volatility of ClF (b.p. -100°C) suggests that little or no association or self-ionization (to Cl^+ and ClF_2^- ions or to Cl_2F^+ and ClF_2^- ions) exists, but the electrical conductivity is higher than that of ClF_3. Chlorine monofluoride is prepared by reaction of ClF_3 and Cl_2.

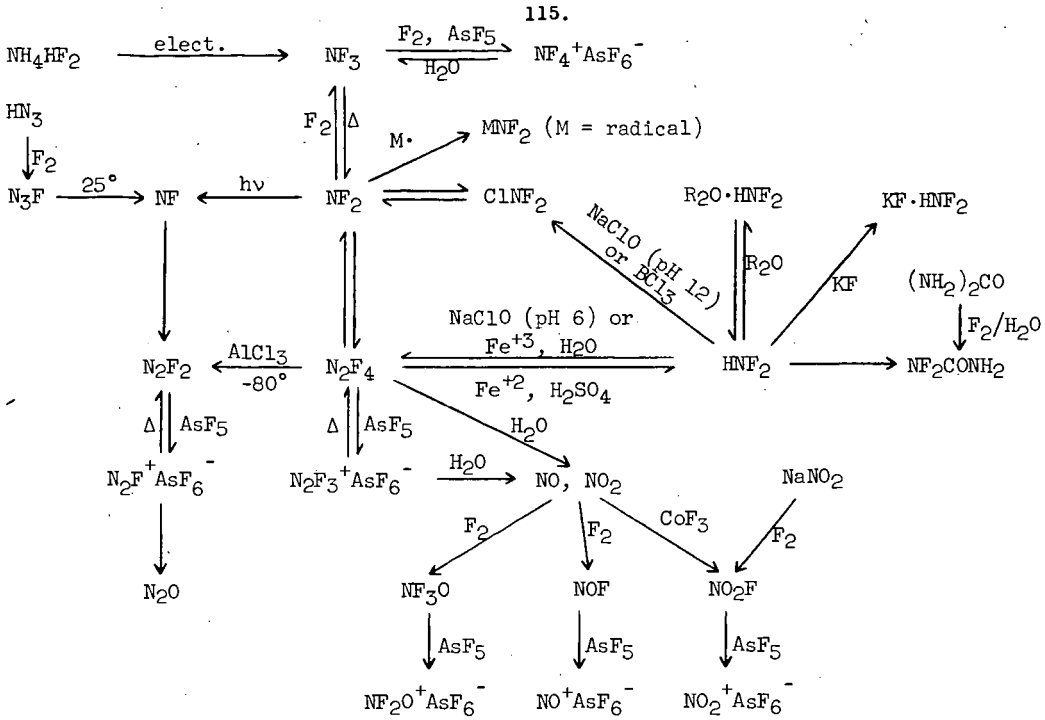


Figure 3 - Interconversion of Nitrogen Fluorides

TABLE III

PROPERTIES OF HALOGEN FLUORIDES AND DERIVATIVES

Compound	MP, °C	BP, °C	NMR	IR
ClF	-154 ± 5	-100.8	440	793, 785
ClF_3	-76.3	11.75	-14(a), -123(e)	761, 746, 713, 694
ClF_5	-103 ± 4	-14	-412(a), -247(e)	786, 732, 541, 486
BrF_3	8.8	127	39	674, 613, 384, 300
BrF_5	-60.5	40.8	-132(e)	683, 644, 587, 369
IF_5	8.5	97.0	-53(a), -4(e)	710, 640, 318
IF_7	4.8[a]	4 (1 atm.)	-177 (-168)	670, 547, 426, 368, 250
ClO_2F	above -115	-6	-329 (330)	1270, 1259, 1104 (pqr) 632, 548
ClO_3F	-146	-46.8	-287	1315-1300, 725, 717, 714, 590
IF_5O	4.5	--	--	--

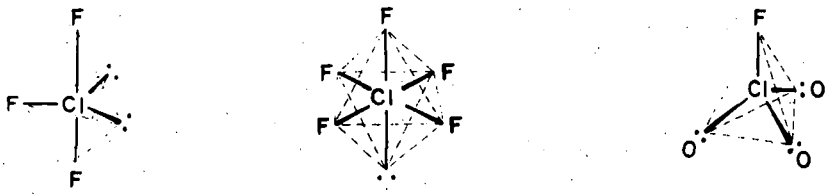
a Triple point 6.4.

Chlorine trifluoride is usually described as having a T-shape, but is better regarded as a trigonal bipyramid derivative. The two apical Cl-F bonds are elongated (1.70 Å) compared to the equatorial Cl-F bond (1.60 Å). The bond angles are 87.5° and 175°. The ^{19}F NMR of gaseous ClF_3 shows the apical fluorines to be further downfield (-145.6 ϕ) than the equatorial fluorine -19.7 ϕ. In liquid ClF_3 (with HF carefully removed) the resonances are -159.0 and -21.8 ϕ. The high dipole moment determined with the liquid (1.00-1.03 D) compared to that in the gas (~ 0.6 D) suggests considerable interaction and the relatively low volatility (b.p. 12°) confirms this, but the electrical conductivity shows that this interaction is essentially not in the form of self-ionization to ClF_2^+ and ClF_4^- ions. Evidence for some dimerization in the gas has been suggested. However stable salts of both of these ions are known, e.g., $ClF_2^+SbF_6^-$ and $Cs^+ClF_4^-$. Chlorine trifluoride is commercially available in quantity, being prepared by fluorination of chlorine. It is an extremely vigorous fluorinating agent, but can in turn be fluorinated to ClF_5 under pressure. Moisture converts ClF_3 to ClO_2F and ClO_2.

Chlorine pentafluoride is the newest member of the halogen fluoride family and has very recently become available commercially in laboratory quantities. It is prepared by the high pressure fluorination of ClF_3 or a salt such as $CsClF_4$ at 150° or above. It has also been prepared by the fluorination of ClF_3 under ultraviolet radiation or electric discharge at low temperatures and by platinum hexafluoride. The structure of ClF_5, a square pyramid, is an octahedral derivative with the apical Cl-F bond length of 1.62 Å and the equatorial bonds 1.72 Å. The ^{19}F chemical shifts are -412 ϕ (apical fluorine) and -247 ϕ (basal fluorines). The former is one of the most unshielded fluorine atoms known, being exceeded only by those in F_2, O_2F_2, and NOF. The dipole moment is probably 0.2-0.4 D. The boiling point indicates very little interaction exists in the liquid and self-ionization is not expected. The ClF_4^+ ion is an intense peak in the mass spectrum and the possibility of obtaining

stable salts such as $ClF_4^+SbF_6^-$ appears reasonably good. The addition of fluoride ion to ClF_5 to give ClF_6^- does not appear likely (although BrF_6^- salts have been reported) since the chlorine atom would be pseudo-heptacoordinate and this type of coordination is without precedence in elements of the second row of the Periodic Table.

The structures of ClF_3, ClF_5, and ClO_3F have been determined and are shown below.



The commercially available higher halogen fluorides are BrF_3, BrF_5 and IF_5, with IF_7 available on special order. Bromine trifluoride is structurally and chemically very similar to ClF_3 except that self-ionization is extensive in liquid BrF_3:

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Bromine trifluoride has therefore an exceptionally high boiling point (126°) and electrical conductivity. It is an excellent solvent for many ionic materials. Stable salts of both the BrF_2^+ and BrF_4^- ions are known, but in some instances with BrF_2^+ the complexes may be fluorine bridged rather than truly ionic. Bromine pentafluoride and iodine pentafluoride are also structurally similar to ClF_5. Self-ionization occurs to an appreciable extent in IF_5, but far less in BrF_5.

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

Stable salts have been reported for BrF_4^+ and BrF_6^- as well as for IF_4^+ and IF_6^-, but structural studies are incomplete. Unlike BrF_5 or ClF_5, IF_5 undergoes fluorine exchange with HF. The BrF_3 and BrF_5 are quite energetic fluorinating agents. While IF_5 is a considerably milder fluorinating agent, it inflames or forms explosive mixtures with many organics. It can be dissolved in excess of such solvents as sulfolane, but forms crystalline complexes with certain oxygenated solvents such as dioxane.

Iodine heptafluoride is formed by the reaction of IF_5 with F_2 at about 100°. The dissociation of IF_7 to IF_5 and F_2 sets in at higher temperatures, ~300°, and ΔH_{dissoc} is 28.5 kcal/mol. The structure of IF_7 in the gas phase is the pentagonal bipyramid, but the structure in the solid is still uncertain. The ^{19}F NMR of the gas is a singlet (ϕ = -336 ppm) suggestiong intramolecular exchange. (The spectrum of the liquid is a doublet at lower temperatures, a singlet at higher temperatures because of quadrapole effects.) The symmetrical structure of IF_7 gives it an extremely short (~2°) liquid range (sublimes, 4.77°; triple point, 6.45°). The reaction of IF_7 as a fluorinating agent are much more vigorous than those of IF_5. With strong fluoride acceptors IF_7 forms salts such as $IF_6^+AsF_6^-$. No reaction to

form such salts as $Cs^+IF_8^-$ have been reported, but the fluorine exchange which occurs between HF and IF_7 in the gas phase may involve a HIF_8 or a IF_6HF_2 intermediate.

The halogen fluoride oxides of major interest are ClO_2F and ClO_3F, but BrO_2F, IO_2F and IF_5O have been characterized. Only perchloryl fluoride, ClO_3F, is commercially available. Chloryl fluoride, ClO_2F, is readily prepared by allowing ClF_3 or ClF_5 to stand with excess of a chlorate or chlorite salt in a Monel cylinder:

$$2ClF_3 + 3NaClO_3 \xrightarrow{25°} 3ClO_2F + 3NaF + Cl_2 + 1.5O_2$$

$$ClF_5 + 3NaClO_2 \xrightarrow{25°} 2ClO_2F + 3NaF + Cl_2 + O_2$$

(The O_2 and Cl_2 are removed at -80°.) The ClO_2F is also formed by the reaction of ClF_3 or ClF_5 with traces of moisture, but is in turn readily hydrolyzed with additional water. The ClO_2F is isoelectronic with PF_3 and SF_2O and should have approximately the same structure, i.e., a tetrahedral arrangement with an electron pair at one apex. The ^{19}F NMR shows the fluorine atom far downfield, ϕ = -332 ppm. This structure makes ClO_2F an extremely reactive oxidizer. It is in turn fluorinated only with difficulty to ClF_5. The ClO_2F undergoes the fluoride abstraction reaction to give stable salts such as $ClO_2^+AsF_6^-$, but efforts to form such salts as $Cs^+ClF_2O_2^-$ have not been successful. Pyrolysis of ClO_2F at 300° and 0.5 atm. pressure gives ClF and O_2 apparently via an intermediate ClFO species.

Perchloryl fluoride has a closed tetrahedral structure with the approximate parameters: Cl-F, 1.55-1.60 Å; Cl→O, 1.40 Å, dipole moment 0.023 D. The ^{19}F NMR shows the fluorine at ϕ = -287 ppm. The structure of ClO_3F gives it considerable kinetically derived stability and it is relatively unreactive at mild temperatures, e.g., it does not hydrolyze, or react with sodium. Above 150° ClO_3F is a potent oxidizer for most organics and attacks many metals in the presence of moisture. Attempts to react ClO_3F with fluoride acceptors such as AsF_5 have not led to stable salts, but the $AlCl_3$-catalyzed reaction of ClO_3F with aromatics (to give $ArClO_3$ compounds) likely involves an intermediate ClO_3^+ ion. No reaction between CsF and ClO_3F has been effected and ClO_3F is quite resistant to fluorination. With NH_3, ClO_3F is converted to $NH_4^+NHClO_3^-$, from which metal salts such as $KNHClO_3$ and K_2NClO_3 can be prepared. All of these salts are shock sensitive. Perchloryl fluoride is generally quite soluble without reaction with other oxidizers and has a small (0.5-5 g/liter) solubility in organic solvents and water.

Bromyl fluoride BrO_2F (formed by the reaction $KBrO_3$ or BrO_2 and BrF_5 at -50°) is thermodynamically unstable and has been studied very little. Of the reported iodine fluoride oxides, only IF_5O appears to be unequivocally established as a molecular entity. It is readily formed by reaction of IF_7 with traces of moisture or with glass and has a relatively low reactivity because of the nearly octahedral structure. The remaining iodine fluoride oxides, IF_3O, IO_2F and IO_3F are all white crystalline solids and may not be molecular entities. The "IF_3O" and "IO_2F" can be prepared by reacting I_2O_5 respectively with IF_5 and F_2. The pyrolysis of IF_3O gives IO_2F and IF_5 and the observed reversibility of this reaction suggested the ionic structure $IO_2^+IF_6^-$ for IF_3O. The IO_2F may exist in a bridged form or possibly in the ionic form, $IO_2^+IF_2O_2^-$, since stable salts of both of these ions are formed. The IO_3F (formed by fluorination of periodic acid in HF) is reported to undergo hydrolysis slowly and thus may in fact be structurally analogous to ClO_3F.

Suggestions for Additional Reading

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DETONABILITY TESTING AT NONAMBIENT TEMPERATURES AND PRESSURES

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ABSTRACT

The generally adopted method for measuring the susceptibility of sensitive liquids to shock is described by the Chemical Propellant Information Agency in the publication "Liquid Propellant Test Methods."[1] The recommended test is limited to use under ambient conditions of temperature and pressure and relies only upon the damage to a witness plate as the criterion for detonability. This report discusses modifications to the test procedure which retain sample size and geometry but permit studies over the ranges of 77°K to 373°K at 1 atm to 10 atm. This broader applicability reduces the value of witness plates--always somewhat dubious. Therefore two other methods have been evaluated, both of which measure detonation velocity: one is electronic, and the other utilizes an explosive witness. The revised test satisfies the requirements for an extended range sensitivity test for use with high energy liquids.

I. INTRODUCTION

High energy liquids are often exposed to conditions, such as extremes of temperature and pressure, which may change their susceptibility to shock initiation. Moreover, many high energy materials are condensed only under such extreme conditions. There exists a need for a detonation sensitivity test applicable to these situations. This report describes equipment and outlines procedures to adapt the current JANAF test[1] for use under the following conditions:

$$77^{\circ}K < T < 373^{\circ}K$$

$$1 \text{ atm} < P < 10 \text{ atm}$$

The two methods used measure detonation velocity, in contrast to the JANAF method which utilizes only damage to a witness plate to determine whether detonation occurred. The first (and perhaps the simpler) technique is an adaptation of D'Autriche's method.[2] In this method, shown schematically in Fig. 1, the detonation velocity of the unknown sample in the test cup is compared with that of an explosive sheet of

known detonation velocity on the witness plate. The tetryl booster initiates the mild detonating fuze (MDF) which in turn initiates the explosive sheet at the "start" position. This detonation propagates farther along each finger of the explosive sheet. The other end of each finger of the explosive sheet is initiated via the detonation probes by the strong wave traveling through the test cup. The detonation waves that collide within the fingers of the sheet explosive create dents in the witness plate that are deeper than those left by a unidirectional wave. The result of a typical shot is shown in Fig. 2. From the position of the dents and the properties of the system, the wave velocity within the sample can be calculated (see Appendix A). Although a strong wave from the tetryl booster traveling through the liquid or the cup may initiate the probes, detonation is detected by a constant velocity.

The second method utilizes a resistance wire in the detonation cup and a constant current power supply to provide a continuous detonation velocity record on an oscilloscope. This method is considerably more precise. It requires a modest amount of electronic equipment and considerable skill on the part of the user. The equipment and operating procedures are adequately described elsewhere[3] for solid explosives; modifications for adaptation to liquid testing under the conditions described above are included in this report.

Details of either method will vary with the properties (e.g., toxicity, vapor pressure, etc.) of the compound tested. In the following paragraphs, procedures employed with two compounds (N_2F_4 at low temperatures and $C_2H_5ONO_2$ at elevated temperatures) are described; other materials may require changes in design and in operational procedures.

Before attempting to determine the detonability of high energy materials it is important that persons who lack experience with explosives be thoroughly educated in the safe handling of explosives. Reference 1 lists many of the standard references for explosive handling. It is imperative that heated or cryogenic pressurized systems be considered as less predictable than systems at ambient conditions until detonation parameters are firmly established. Remote handling should be the rule because, even though the test liquid may not be extremely sensitive, sensitization of the booster and explosive train may occur. High energy oxidizers may also ignite the explosive train and cause premature detonations.

II. TEST EQUIPMENT

A. Cup

The liquid under test is held in a cylindrical metal cup closed at one end with a metal diaphragm soldered in place; the other end (the

top) is closed with caps which contain instrument probes. The cup is fabricated as follows: Each end of a section of 1" Schedule 40 extruded steel pipe (or other metal compatible with the test liquid) is faced on a lathe to an overall length of 6.0".

For the modified D'Autriche method, the cup is prepared as shown in Fig. 3. A 2.0-mil-thick stainless steel diaphragm 2" in diameter is centered and silver-soldered on the bottom of the cup. If the cup is to contain a cryogenic, toxic material or a substance which is not compatible with the atmosphere, the top must be sealed and special transfer lines must be installed.

For materials that are transferred in vacuum lines, the cups are threaded with 1" standard taper pipe threads. Two holes are drilled 3/8" below the last thread to accommodate 1/4" o.d. tubing. Two 1' pieces of 1/4" o.d. tubing are soldered in the holes so that the soldered ends are flush with the inner wall of the cup.

B. Caps

The caps, prepared from 1" pipe caps, support the necessary instrument probes for temperature measurement, liquid level sensors[4] and the continuous wire probes. The simplest test, using the modified D'Autriche method with a liquid such as ethyl nitrate which can be poured into the cup, requires only a pipe cap and no probes. For materials to be tested at nonambient conditions and to be transferred in a vacuum line (cryogenic materials and toxic materials) or for tests utilizing the continuous wire, instrument probes are installed in the cap.

For installing thermowells, a 1/8" hole is drilled into the cap and a length of 1/8" tubing extended through the cap. This tubing is cut and positioned to extend no farther into the cup than 2" above the bottom diaphragm when assembled and soldered to the cap. The bottom of the thermowell is closed and sealed with solder. The end outside the cup is left open for inserting thermocouples; a series of couples at different levels may serve as liquid level sensors. For caps that require resistance wire leads or thermistor leads, holes are drilled in the cap to accommodate insulated metal-to-ceramic electrical leadthroughs. These seals are soldered in place, preferably with a lower melting solder than that used for the thermowell. Two such seals, or a double seal, can accommodate a thermistor.

For the resistance wire and supporting bow, two holes are drilled in the cap. One, in the center of the cap, is drilled to contain an insulated electrical leadthrough. Approximately 1/4" from the center of the cap, another hole is drilled to hold the resistance wire support. This support is fabricated from a 1/16" rod long enough to extend through the cap into an assembled cup to a distance of less than 1" from the diaphragm. Both the rod and the electrical leadthrough are soldered in place. At a distance of 1/2" from the end, the rod is bent 90° toward the center of the cap. From the end of this rod to the electrical lead

on the cap, a length of 1-mil resistance wire is strung and the wire is anchored well at both positions to give good electrical contact. An assembled cup showing modifications for both the D'Autriche method and the continuous wire method is shown in Fig. 3. It is not necessary that all parts shown be used in every test.

C. Temperature Control of Cup

Under nonambient conditions it is advisable to use liquid baths around the test cups to control temperature along the entire cup. A convenient way to attach a leakproof metal container around the cup is to cut a 1-1/2" hole in the bottom of a high 6" diameter metal can and to solder the overlapping diaphragm of the detonator cup into the hole as shown in Fig. 3. Commercial 3-lb coffee cans have been satisfactory.

Above ambient temperatures, the bath is heated with heating tapes or inexpensive immersion heaters. For cryogenic materials, the cup is filled with the appropriate coolant--dry ice, liquid nitrogen, liquid argon, liquid oxygen, etc. Insulating materials may be used around the bath.

D. Bath Materials

It is extremely important to give careful consideration to the bath materials because they must be inert to all materials used in the shot. Oil baths are likely to contribute to fire hazard; spilled solvents or vapors may react with or sensitize the explosive train materials, and mixtures of solvents may be detonable.

E. Detonator and Booster

An explosive wire detonator is followed by 18" of Primachord. The Primacord in turn is followed by a small RDX pellet and the booster. The booster charges used for the temperature range from -196 to 100°C consist of two 1" x 1-5/8" diameter tetryl pellets, density about 1.56. For the higher temperature (100° to 150°C), higher melting HMX pellets may be substituted (m.p. 270° to 280°C).

F. Detection Equipment

1. Resistance Wire Method

The procedure for determining detonation velocity is fully described in Reference 3.

2. D'Autriche Probe Assembly

For each shot a test cup is prepared as shown in Fig. 3 and aluminum witness plates are prepared as shown in Fig. 4a. Using a razor blade,

five pieces of MDF, each 20.00" long, are cut on a piece of wood or Micarta. Five 1/2"-wide strips of sheet explosive are also cut, one about 4" long and the others 8.00". Using precise scales and squares, the short strip is cemented parallel to the short edge of the plate with one end over the single hole. The long strips are cemented parallel to each other, one end over each of the remaining four holes and the other end over and in contact with the short strip (see Figs. 4b and 5).

The test cup and booster are assembled as shown in Figs. 1 and 5 and the witness plate is secured nearby. One end of each of the 20" lengths of MDF is inserted through a hole in the plate until it contacts the explosive sheet (Fig. 4b). The other ends are put in place on the charge (no auxiliary booster is used) as shown in Figs. 1 and 5, four or more along the cup wall and one to the initiator. All ends are cemented securely in place.

G. Support Stand for Detonator, Charge, and Cup

A suitable frame is constructed to support the assembled charge. The detonator, booster, and cup are aligned and held in place with adhesive tape. The assembled shot and cup are later placed on the support stand and tied into place with adhesive tape. At elevated temperatures a noncombustible tape should be used.

H. Vacuum Transfer Equipment

For remote handling of volatile, toxic, or cryogenic materials which cannot be conveniently transfered in a simpler manner, a vacuum system is constructed (see Fig. 6). This system, which is suitable for fluorine oxidizers, was used for testing the detonability of N_2F_4. A fluorine tank is used for passivation of the system before testing high energy fluorine oxidizers. The system is designed to permit isolation of the supply tank from the detonator test cup to prevent possible detonation through the lines to the main supply tank. The lines are flushed with an inert gas after the transfer is completed. The system also contains a measuring bottle of sufficient volume, when filled with test material at a predetermined pressure, to exactly fill the cup with condensed liquid.

To prepare the system, the valves and other parts (components are described below) are completely disassembled and each is cleaned. Defective gaskets and parts are replaced. If the valves are to be soldered or welded to the transfer lines, the gaskets are left out of the valves until this operation is complete. To remove borax-type fluxes it may be necessary to steam-clean the soldered joints. Valves 1 through 6 (Fig. 6) and the solenoid operators are assembled and mounted on a small portable metal panel; enough tubing (1 to 2 feet) is attached to valves that lead to other components, tanks, pumps, and gauges so that connecting lines can later be installed on these ends without interrupting the

valve-panel system. This section should be leak tested before final assembly at the test site.

1. Vacuum Equipment Components

Valves 7 and 10 (Fig. 6) are Chlorine Institute valves available from Superior Valve Company, Pittsburgh, Pennsylvania (Fluorine Cylinder Valve Cat. No. 1214F). Valves 8 and 9 are conventional as supplied by the vendor. All other valves are Hoke Cat. No. 30206-6, with No. 80065-1 solenoid operators. These ball valves operate smoothly and thus may be less likely to initiate an explosion than would a solenoid-operated needle valve which operates more abruptly. The vacuum pump is a conventional, low-capacity, laboratory model filled with fluorocarbon oil but powered with a 1 h.p. motor for easy starting. All transfer lines are copper tubing, silver soldered to valves and fittings. The test cup assembly is 1" Schedule 40 pipe, surrounded by a can cooled with dry ice.

2. Operating Procedure

For remote transfer of a test sample from the supply tank, the following procedure is used: With valves 1, 7, 8, and 9 closed and all others opened, evacuate system. Close all valves. Open valve 10. Open valve 7. Open valve 2. Fill measuring bottle to desired pressure as indicated on gauge. Close valve 2. Close valve 7. Open, in order, valves 1, 3, and 7; this flushes this section with helium and serves to isolate the supply tank from the measuring bottle. Open valve 4. Essentially all of the N_2F_4 or other test material in the measuring bottle should condense in the test cup. Completeness of condensation is judged with the thermistor and thermocouple liquid level detector or by an appropriate pressure drop in the system. In this operation the test cup acts as a trap. Should any noncondensables interfere, they may be removed through the pump by briefly opening and pumping through valve 5. The preset needle valve prevents surging or splashing of liquid. Close valve 4 and the cup is ready for the test.

I. Auxiliary Breathing Air Supply

To test toxic materials and protect operating personnel from dangerous fumes, protection equipment and an auxiliary air supply should be available. Portable self-contained air or oxygen breathing equipment is suggested.

III. FINAL ASSEMBLY

The prepared cups and caps containing the desired instrument probes, transfer lines, vacuum components, gauges, and instruments are assembled and checked at the test site. The test cup and shot assembly are positioned in the firing chamber to minimize damage to the lead lines and

auxiliary equipment. For convenience in repeating shots, the cups are attached to the transfer lines with quick-disconnect fittings.

It is advisable to schedule a preliminary test with an inert material of very nearly the same physical properties as the test material, to check the reliability of the equipment and gain experience in operating the system. Also, materials of known detonation characteristics should be tested for comparison.

When the assembled equipment has been checked, the test material supply tank is attached to the vacuum line and the transfer lines are evacuated up to the supply tank valve. Since most of the transfer lines are extremely small, several minutes may be required to pump the transfer system down to a desirable pressure (10 to 50 microns). This time can be employed to assemble the detonation train and D'Autriche witness plates (if used).

The first explosive attached to the equipment is the D'Autriche witness plate and assembly, if used. The MDF probes leading from the cup must be carefully positioned and firmly held to obtain maximum separation, thus preventing "shorting" of the shock train between probes. With the witness plate and probe assembly firmly secured to the test stand, the booster, detonator, and Primacord are assembled and the booster is placed flat against the diaphragm on the cup. The entire assembly is held together on the stand with adhesive tape. If the shot is to be heated, noncombustible tapes should be used. The electrical leads to the instrument panels are installed and checked.

If it is possible to pour the test liquid into the detonation cup (i.e., if the material is nontoxic and the shot is to be done above ambient conditions), no vacuum transfer equipment is used. This is the procedure with ethyl nitrate tested above ambient conditions. In this case one of the two side-arm tubes on the cups is closed with a quick-disconnect plug after the cup is filled. The liquid should not be allowed to wet the plug and quick-disconnect fittings when they are being closed, since this may cause premature detonation. The second tube arm of the cup serves as a lead to determine pressure in the system.

With the shot assembled and the transfer system evacuated, the remote control valves are closed. Next, the coolant or bath liquid is placed around the cup. This should be done remotely, if possible. The valve on the sample tank is opened to allow the gas to flow to the remote control valves only. The remainder of the transfer operation is completed as outlined previously. When this is complete, as judged by one or all of the methods used to determine the liquid level in the cup, the supply tank is isolated from the shot by inert gas in the transfer lines and the shot is fired.

IV. DETERMINATION OF THE DETONATION VELOCITY

A. D'Autriche Method

A failing (i.e., nonpropagating) detonation wave is detected by a decelerating wave velocity rather than by failure of the MDF. The strong shock from the tetryl booster usually initiates the MDF when the cup contains a nondetonating liquid. Positive results are reported when a constant velocity wave front is established. The method does not readily detect transient changes in detonation phenomena but has the advantage that a record is obtained on the plate even when nondetonating material is tested in the cups.

Appendix A outlines the procedure for determining detonation velocity from data obtained with plates. Reliability in calculating detonation velocity is believed to be approximately ±10%

B. Continuous Wire Method

This method, developed for solid cast explosives, is adequately described in the literature.[3] The cup and booster charge described replace the solid explosive. This method has the advantage of producing a continuous record of shock disturbances in the test liquid but does not produce a record when the material does not detonate.

V. TEST RESULTS

The procedure presented in this paper should yield results both reliably and safely. Each component and step has been evaluated by the authors in frequent tests with N_2F_4, O_3F_2, or $C_2H_5ONO_2$. The procedure was then used to determine the detonability of these three compounds as liquids. The results for O_3F_2, published elsewhere,[5] established the nondetonability of this liquid which is stable only below $\sim 100^\circ$K. N_2F_4, b.p. 200°K, was tested from 195°K to 213°K ($\sim 10^3$ torr). Several tests were run with the continuous wire method; all gave typical negative results. The one test run with the explosive witness showed the shock velocity decaying from an initial value of ~ 2.8 mm/μsec to a final value of ~ 1.5 mm/μsec. Again, this is characteristic of a nonpropagating shock. To evaluate the test at the other environmental extremes a hot liquid, ethyl nitrate ($C_2H_5ONO_2$), was used at high pressure. Although some difficulty was encountered because of the tendency of the liquid to detonate spontaneously above its boiling point, four successful continuous wire tests were conducted from 97° to 114°C and up to 175 psig. Each indicated, again with typical records, that the liquid is detonable.

Although these were the only shots conducted with the exact procedure defined by this paper, many were run under conditions only slightly different; generally these affected safety and simplicity rather than

reliability. Details of most of these are available to the reader of the project reports (q.v.).[6] Important conclusions are that the tests, as described, reliably detect detonation and, equally reliably, non-detonation. Low velocity detonations are probably included in the latter. The results have been proven to be independent of either temperature or pressure. For example, incidental tests demonstrated that MDF detonates with a velocity invariant with temperature.

In summary, the authors present the procedure described in this report with confidence that, if used as described, it will serve as a useful, worthy supplement to the Liquid Propellant Test Method No. 1.

VI. ACKNOWLEDGEMENT

The test procedure described in this report was developed as a part of research generously sponsored by the Office of Naval Research.

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Appendix A

ADAPTATION OF THE JANAF BOOSTER TEST: DATA REDUCTION

The equation for reducing the data from the witness plates is derived as follows. Assume the following:

1. There is a small, finite, but reproducible time for a detonation to propagate across explosive interfaces. This is frequently referred to as an "induction time."

2. The time required for two detonations originating at a common point and meeting at a point x is the same for two corresponding paths.

3. The detonation velocity of explosives is a reproducible function of environment.

The nomenclature used in the equation is as follows:

P = lengths of MDF; the subscript denotes the particular branch

P_b = length of MDF from tetryl booster than initiates the explosive on witness plate

V = detonation velocity of any P with corresponding subscript

V_s = wave velocity within sample

V_w = detonation velocity of standard explosive used

L = distance between opposing points of initiation for each sheet explosive finger

x = point at which detonations meet; measured from MDF

ds' = distances between MDF on sample cup

dw' = distances between corresponding strips of explosive on witness plate

ds = distance from tetryl pellet for first MDF

dw = distance from the start to strip 1 on witness plate

μ, η = small, unknown, but reproducible delay or induction times in transition from cup to MDF and MDF to EL-506-D

The time required for the detonation to travel from the tetryl through the sample cup, the first "finger" of MDF and to point x_1 in the sheet explosive is:

$$t_1 = \frac{ds}{V_s} + \mu + \frac{P_1}{V_1} + \eta + \frac{x_1}{V_w} \qquad \text{(A-1)}$$

The time required for the detonation to travel from the tetryl through the "start" branch of the MDF and to x_1 through the sheet explosive from the opposite direction is:

$$t_1' = \frac{P_0}{V_0} + \eta + \frac{dw}{V_w} + \frac{L - x_1}{V_w} \qquad \text{(A-2)}$$

Equating (A-1) and (A-2) and rearranging terms:

$$\frac{ds}{V_s} = \frac{P_0}{V_0} - \frac{P_1}{V_1} + \frac{dw}{V_w} + \frac{L - 2x}{V_w} - \mu \qquad \text{(A-3)}$$

Similarly, by equating the times of travel from the tetryl to point x_2 in the second finger of sheet explosive:

$$\frac{ds + ds'}{V_s} = \frac{P_0}{V_0} - \frac{P_2}{V_2} + \frac{dw + dw'}{V_w} + \frac{L - 2x_2}{V_w} - \mu \qquad \text{(A-4)}$$

Subtracting (A-3) from (A-4) and noting that $P_1 = P_2$ and $V_1 = V_2$:

$$\frac{V_s}{V_w} = \frac{ds'}{dw' + 2(x_1 - x_2)} \qquad \text{(A-5)}$$

V_s, ds', and dw' are conditions of the experiment; x_1 and x_2 are measured; therefore V_s can be calculated.

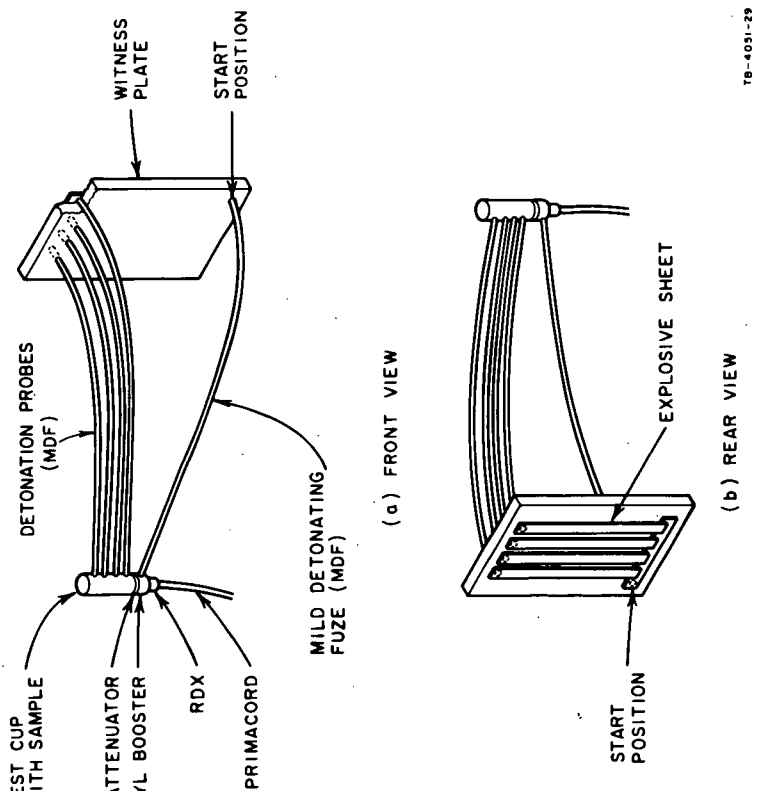


Fig. 1 Modified D'Autriche Assembly

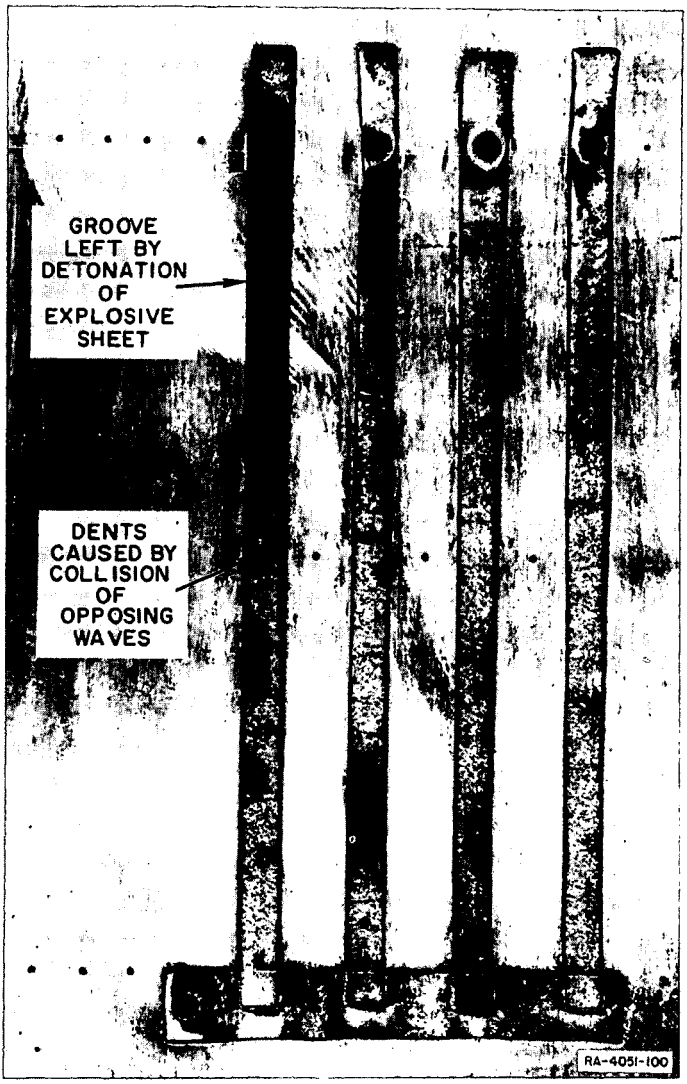


Fig. 2 Typical Witness Plate

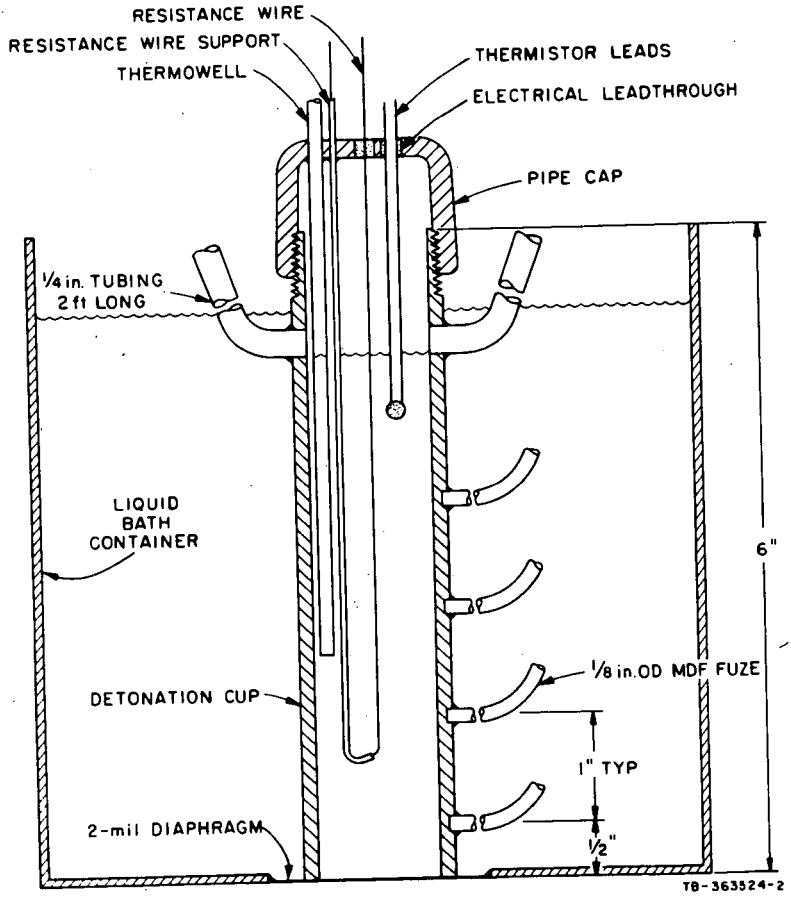
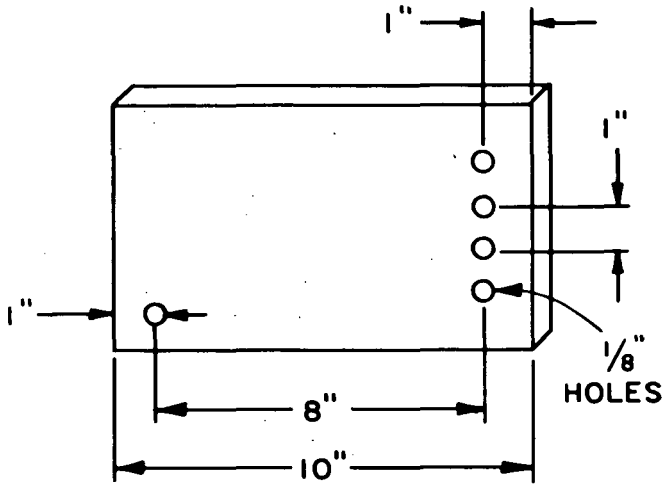
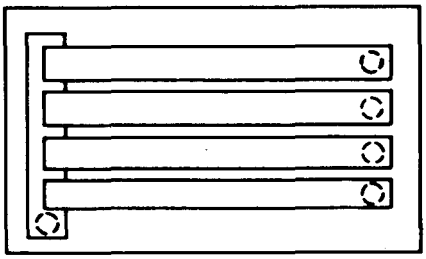


Fig. 3 Detonation Cup



(a) ALUMINUM WITNESS PLATE



(b) SHEET EXPLOSIVE ON WITNESS PLATE

TA-363524-1

Fig. 4 Witness Plate Details

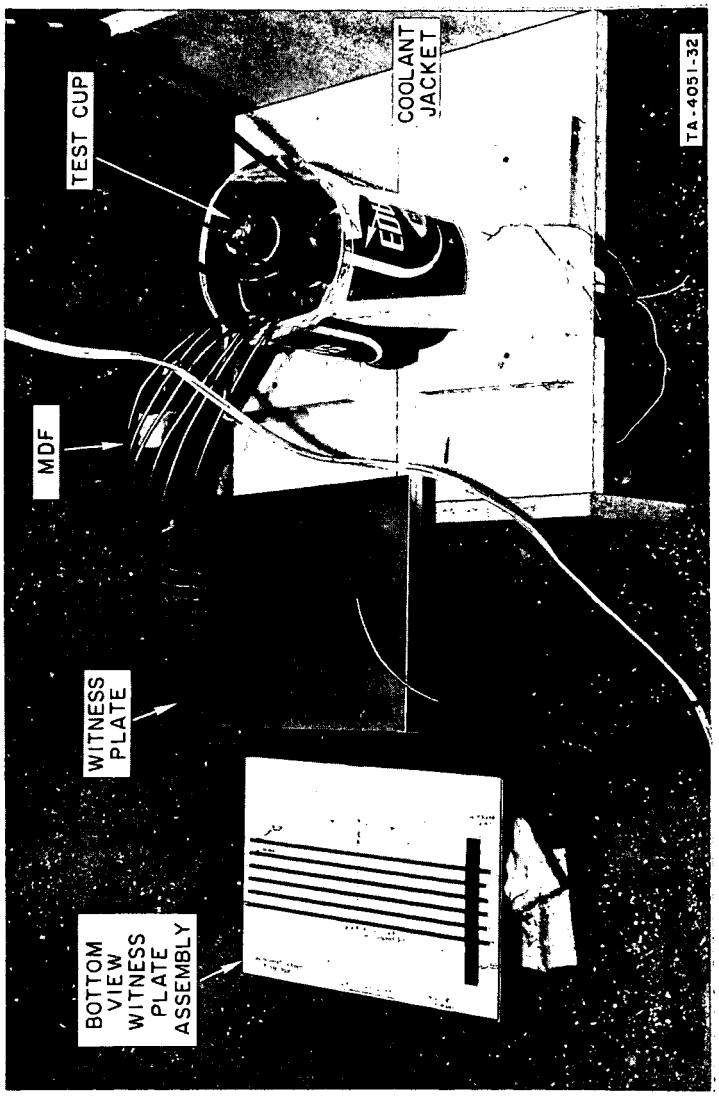


Fig. 5 Assembled Detonability Equipment

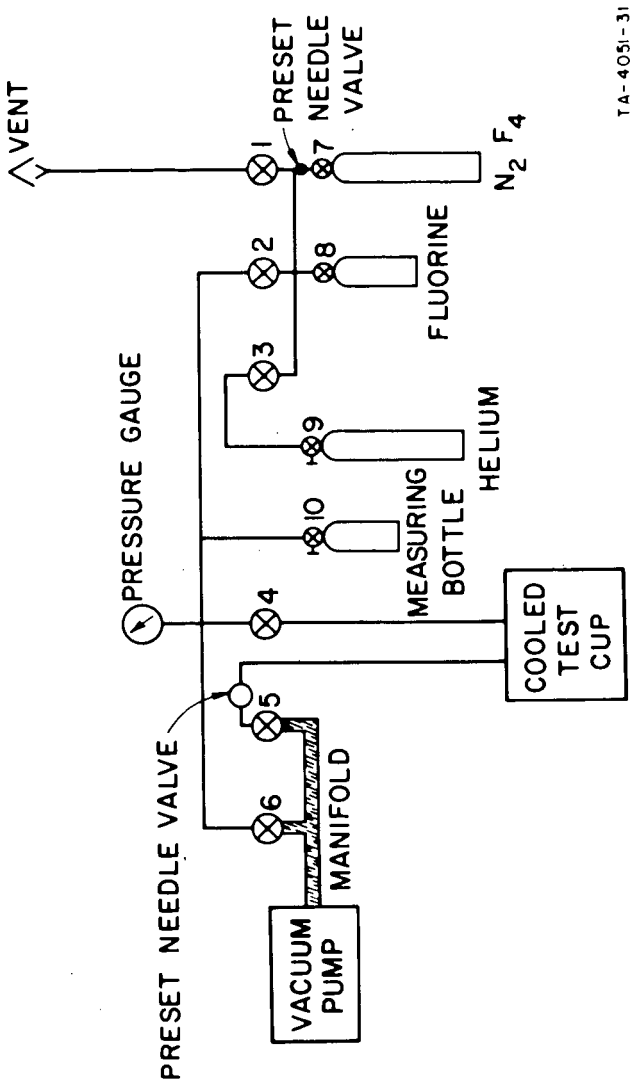


Fig. 6 Vacuum Transfer Line